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Soil Type and Management Effects on Organic Carbon Stocks and Soil Structure Quality in North Germany.

Rainer Horn*, Anneka Mordhorst*, Heiner Fleige*,
Iris Zimmermann*, Bernd Burbaum**, Marek Filipinski**
and Eckhard Cordsen**

*Institute for Plant Nutrition and Soil Science, Hermann Rodewald str. 2, 24118 Kiel, Germany.

**State Agency for Agriculture, Environment and Rural Areas of the German Federal State Schleswig-Holstein (LLUR)

Corresponding Author: Rainer Horn, e-mail: rhorn@soils.uni-kiel.de

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Abstract

Improvement of carbon sequestration in soils for a more sustainable environment and prevention of climate change require not only knowledge about soil organic carbon (SOC) stocks, but also about interactions between land use and total amount and distribution of carbon. In North Germany (state: Schleswig-Holstein) about 925 soil profiles in the four dominant geological regions [Weichselian glacial region, the sandy outwash region (Lower “Geest”), the Saalian glacial region (Higher “Geest”), and the marshland with alluvial deposits] were sampled down to at least the 90 cm depth. Carbon content, pH, bulk density, and grain size distribution were analyzed for the major characteristic soil horizons. The four dominant geological regions possess different SOC stocks as well as SOC contents. The total amount of SOC stored within the representative soil profiles down to the 90 cm depth was analyzed for three depths: 0 – 30, 30 – 60, 60 – 90 cm; for the total area of Schleswig Holstein (15.369 km²), they summed to 244 Mt. SOC stocks, however, differed depending on the land use management system and clay content. Arable soils were most sensitive to soil deformation and the higher the clay content the less rigid they were, if the SOC to clay ratio were used as an index for structural quality. Grassland topsoils showed the highest SOC stocks and a mediate structural quality. The latter was highest for forest soils, which, however, had a higher SOC content but, at the same time, a less fertile SOC composition (litter with high C: N ratio). Further research on the carbon composition (labile, active, intermediate, or passive pools) would help to get a better insight into the role of SOC on soil strength and soil functions.

Highlights:

- SOC stocks of North Germany (Schleswig-Holstein) amount to 244 Mt (0 – 90 cm depth)
- SOC stocks differ depending on the land use management system and clay content
- Highest SOC stocks were found in grassland topsoils (0–30 cm depth)
- SOC:clay content ratio of topsoils defines structure strength of soils

- Arable topsoils showed lower SOC:clay content ratios than grassland and forest ones

Key words: soil organic carbon stocks, land use management, tillage systems, soil strength, SOC:clay ratio, Luvisol, Gleysol, Podzol, Cambisol, Anthrosol.

Introduction

Carbon sequestration, time-dependent changes in soil organic carbon content, or the 4 per mille initiative (4p1000, 2017; IPCC, 2006) are intensely discussed in science and policy because of the worldwide increasing problem of climate change, which has consequences for the environment and human life on earth (van Groenigen et al., 2017; Conrad et al., 2017; Zomer et al., 2017). Carbon stock calculations are done to suggest an improved and more sustainable land use. Alterations of soil management systems in the future will be necessary for increased carbon stocks (Chenu et al., 2019; Cosentino et al., 2006; Balesdent and Arrouays, 1999; Wiesmeier et al., 2012).

Batjes (2016) estimates the worldwide soil organic carbon (SOC) stock to 1400 – 1600 Pg, while Lal (2018) stated that the global magnitude (Pg) of SOC is 677 to 0.3 m, 993 to 0.5m, and 1,505 to 1 m depth. Thus, ~55% of SOC to 1 m lies below 0.3 m depth. He furthermore concludes that alterations of soil management systems in the future will be necessary. The reference points for such calculations are the temporal change in global land use since pre-agricultural understanding natural ecosystems to 2015. However, there are no further details concerning soil type specific variations.

Soil organic matter (SOM) not only helps to improve soil structure formation and soil strength, but it also enhances filter and buffer processes in soils including an enhanced nutrient storage, water availability, and equilibrated heat distribution due to thermal processes (Hartge and Horn., 2016). If an improved soil structure and pore continuity, as well as related hydraulic processes, coincide with higher SOM content and organic carbon quality, they can also help to reduce soil losses due to water and wind erosion. However, the terms carbon sequestration and carbon storage, which are often used in the literature, define different processes. Carbon sequestration describes the process of CO₂ storage in soils, because of plant growth and the decay of organic residues over decades. Carbon stock (storage) quantifies the volumetric changes, because of these long-term processes over depth depending on climatic conditions, parent material, and soil types under various land use systems (Lal, 2004; Wiesmeier et al., 2012; Guggenberger et al., 1994). The increase of the organic carbon stock in soils strongly depends on land use systems (Smucker et al., 2010), while the recommendations on how to ameliorate soil structure and to improve the accessibility and availability of particle surfaces depend on the positive aspects of SOM. The organo-mineral bondings, hydrophobicity, or particle coating with organic acids are of major importance (Horn et al., 2017; Feeney et al., 2006; Blume et al., 2016). The definition of carbon sequestration furthermore assumes that the organic material originates from the site itself and is not added from other sites or as processed material like biochar.

An overview on worldwide research activities concerning soil organic carbon (SOC) stocks was given during the FAO conference in Rome 2017. As an outcome, a SOC stock map was developed and presented during the World Soil Day ceremony in December 2017 (FAO, 2017). This map quantifies the SOC stocks in the top 30 cm of soils worldwide, as the

most dominant but also sensitive soil volume for carbon stock. The world average of about 677 Pg SOC, stored in the top 30 cm of the soil, however, also shows the dilemma, as this layer is most sensitive for management-induced decomposition. Both the ecological as well as economic recommendations assume that additional consideration of the deeper soil layers and a more management specific quantification can help to calculate the SOC storage more reliably, and to describe the effects of SOC on a sustainable soil structure.

SOC stocks can, therefore, be considered twofold: (i) they improve physical, chemical, and biological processes in soils, (ii) these positive effects also depend on the long-term connection between the mineral and the organic phase to be sustainable. Johannes et al. (2017) dealt with the SOC: clay ratio concerning mechanical structure strength and the link to the maintenance of soil functions, and discussed how far SOC stocks can be linked to physical soil properties and functions. They conclude: “the SOC : clay ratio decreases with decreasing soil structure quality. The SOC : clay ratio of $> 1:8$ is the average for a very good structure quality. A SOC: clay ratio of $1:10$ is the limit between good and medium structural quality, thus it constitutes a reasonable goal for soil management by farmers”. This would be a suitable approach, although it is only an indirect link to quantify soil degradation or deformation. In recent years, a new countrywide approach to quantify SOC stocks was introduced in Germany (Walter et al., 2016). It enables SOC stock calculations under well-defined analytical procedures. The benefit of an identical analysis approach coincides, however, with a limited, although well defined, number of soil analyses. They could easily be extended to a smaller scale, if additional, state-based, datasets could be included.

The approach, how to link SOC stocks over depths with qualitative structure classification systems, was hitherto not considered on a state scale with various geological parent materials. However, it may help to define sustainable land use systems on a regional scale (Horn and Kutilek, 2009). It is therefore the aim of this paper to analyze adequate datasets on the state scale in Schleswig-Holstein. How far can site and depth-dependent distributions of SOC under arable, forest, and pasture/grassland management be quantified and linked with soil structure properties expressed as the SOC:clay ratio?

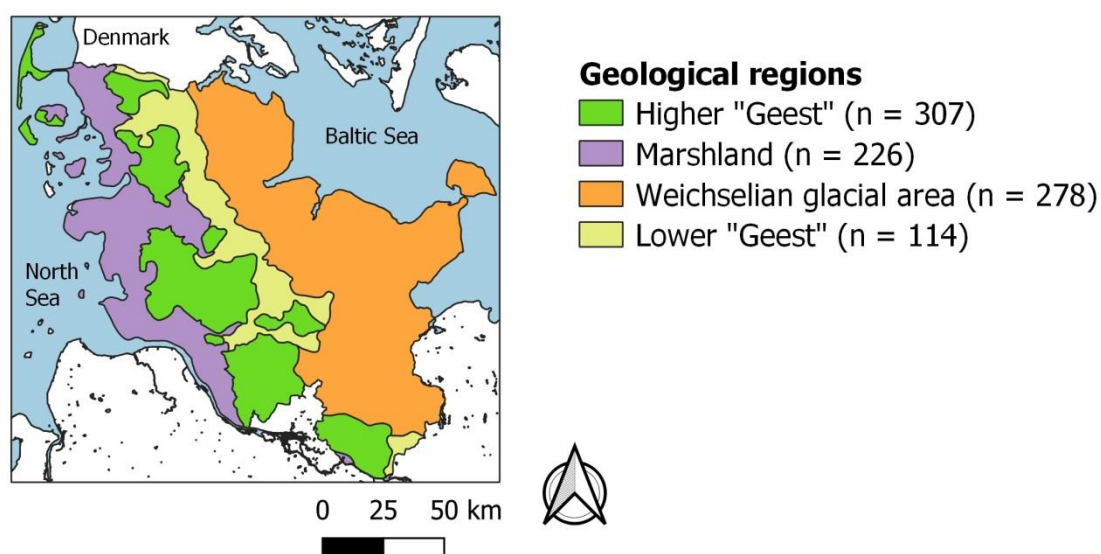


Figure 1. Geographical map representing the 4 geological regions of Schleswig-Holstein (North Germany) with the number (n) of sampled soil profiles. Map basis: BKG (2010).

Materials and Methods

The dataset was collected in between the year 1970 and 2015 during various research programs in Schleswig Holstein by the State Institute of Agriculture, Resource and Landscape Planning (LLUR). It includes 925 soil profiles with a complete soil type description, physical, and chemical data down to at least the 90 cm depth under arable, grassland, and forest land-use. Soil management systems, like conventional and conservation tillage, are also included in the dataset, but they were, unfortunately, not differentiated. Therefore, the corresponding datasets are accumulated using the term “arable land”. The soil samples were collected from the four geological regions of North Germany in the state Schleswig-Holstein (Figure 1): the Weichselian region in the East, the sandy outwash region (Lower “Geest”), the Saalian glacial region (Higher “Geest”) in the center, and the marshland with alluvial deposits in the West of Schleswig-Holstein. The Weichselian glacial deposits contain fertile Luvisols and Cambisols and “Colluvic” Anthrosols, but also Gleysols and lowland Histosols, while the outwash region is dominated by Brunic Arenosols or Cambisols depending on soil texture, Podzols, Gleysols, as well as (Rheic and Ombric) Histosols. The Saalian glacial region is approximately 150,000 years older than the Weichselian region and is characterized by mainly loamy and sandy carbonate free Brunic Arenosols or Cambisols, Stagnosols, Podzols, Gleysols, and Rheic Histosols,. Finally, the marshland includes different types of Fluvic Gleysols, Histosols (the regional distribution and the total area are documented in Table 1). The marsh area involves in total 2,854 km²; the sandy outwash region extends to 2,010 km² the Saalian glacial region to 3,766 km²; and the Weichselian glacial area to 6,740 km². Long-term mean temperature of Schleswig-Holstein is 8.8° C and long-term mean precipitation sum is 840 mm, while the latter averagely decreased from the western coast (marsh, ca. 900 mm) to the eastern coast (Weichselian glacial area, ca. 700 mm) (between 1981-2010, DWD, 2017).

Disturbed and undisturbed soil samples were analyzed, and the data included in this paper like grain size distribution, SOC and bulk density are for soil samples that were taken from different depths, but mostly horizon-specific down to at least 90 cm from all soil profiles. While the methodology remained the same for calculating the bulk density, the techniques for determining the carbon content changed depending on the project over the sampling years (dry combustion for elemental analysis or wet combustion according to the Lichterfelder method as well weighting loss of ignition). For more details see Blume et al. (2010) and Hartge and Horn (2016). SOC stocks (t/ha) were calculated from carbon contents (%) multiplied by bulk density (g/cm³) and soil horizon thickness (cm) and summarized over the depth sections: 0 – 30, 30 – 60, 60 –90 and totally 0 – 90 cm.

Results

- Effect of geological origin, soil type, and land use management on carbon storage.

The four dominant geological regions possess different SOC stocks (Table 1). The total amount of SOC stored within the representative soil profiles down to the 90 cm depth sums up to 244 Mt for Schleswig-Holstein. This sum is limited to the dominant soil types in the four regions, which, in general, cover around 90 % of the total soil surface area of 15,369 km² (Table 1). This resulted in a mean carbon density of 159 t/ha in Schleswig-Holstein. The highly fertile Weichselian glacial area with the largest extent stores the highest amount of SOC followed by the marshland and the higher “Geest” (Saalian glacial area). While 60 – 70 % of the mostly highly fertile soils in the Weichselian glacial area and marshland are mainly

used for crop production (arable land), the less fertile soils of the “Geest” are more represented by permanent grassland and forestry land use (Figure 2). The lowest SOC stocks were calculated for the sandy outwash region, the Lower “Geest”, although the permanent grassland and forest sites are abundant here, which can be attributed to the low storage capacity of the sandy parent material. Within all regions peat soils, like lowland and highland Histosols, always store the largest amount of SOC down to depth. As expected, the total stocks in all regions are always the highest in the Histosols, while, surprisingly, relatively low SOC-stocks were found in the most fertile Luvisols derived from glacial material. Due to the mass movement by erosion, the Anthrosols derived from colluvic material have high amounts of SOC down to the 90 cm depth, which is also the case for (Gleyic) Podzols due to the accumulation of organic acids in the B-horizons. The various forms of Fluvic Gleysols in the marsh region always show high SOC stocks down to depth.

If we compare the overall SOC stock distribution with depth in the Weichselian region, nearly 60 % are stored in the top 30 cm, followed by 25 % in the 30–60 cm depth. The same distribution can be found in the sandy outwash (lower “Geest”), and in the higher “Geest” (Saalian origin). The most equal distribution over depth is visible in the marsh soils due to the geogenic origin of the organic material in the sediments.

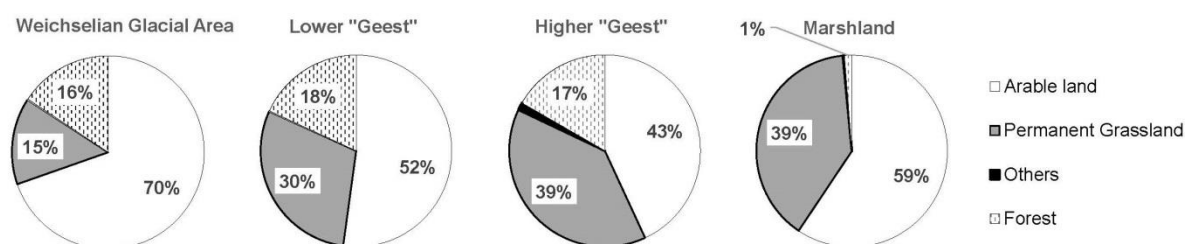


Figure 2. Relative share of the 3 main land use management systems (arable land, permanent grassland, and forest) on the total agricultural and forestry area in Schleswig-Holstein (authors' own representation according to MELUND (2018) and Federal Statistical Office, 2015)

The SOC contents and SOC stocks of the topsoil are related to land use management: arable, grassland, and forest. In all four regions, the grassland topsoils always store the highest amounts of SOC, while the lower and the higher “Geest” also store the highest amounts (Figure 3), with up to 140 t/ha in the top 30 cm in the lower “Geest” area. Significantly, smaller amounts are stored in the arable and forest sites in all four regions.

Table 1. Depth-specific soil organic carbon (SOC) stocks from 0 to 90 cm depth for the most frequent soil types with a relative area > 3 % in the different geological regions in Schleswig-Holstein. *n* = number of soil profiles

Weichselian glacial area															
Soil type (WRB, 2014)	Clay (Mean)	Cla (+/-)	Relative area	Absolute area	0-30 cm		30-60 cm		60-90 cm		Σ 0-90 cm				
					SOC stock	n	SOC stock	n	SOC stock	n					
	[%]	[%]	[%]	[ha]	[t ha ⁻¹]	[Mt*ha]	[-]	[t ha ⁻¹]	[Mt*ha]	[-]	[t ha ⁻¹]	[Mt*ha]			
Stagnic Luvisol	18.6	5.5	23	153662	62	9.5	26	17	2.6	27	11	1.7	26	90	13.8
Stagnosol	20.9	13.3	20	134791	79	10.7	19	19	2.6	24	9	1.3	24	108	14.6
Anthrosol ("Colluvic")	12.4	9.2	16	106485	85	9.0	13	71	7.6	11	49	5.2	14	205	21.8
Cambisol/Brunic Arenosol	4.9	3.3	12	81548	55	4.5	21	15	1.2	26	7	0.5	32	77	6.3
Luvisol	15.4	4.8	8	50547	52	2.6	22	18	0.9	26	9	0.5	28	79	4.0
Rheic Histosol			6	37741	455	17.2	1	204	7.7	5	175	6.6	6	835	31.5
Stagnic Cambisol	9.1	4.5	4	26958	60	1.6	7	17	0.5	5	6	0.2	7	82	2.2
Sum			88	591732	55		109		23	124		16	137		94
Others			12	82222											
Lower "Geest"															
					0-30 cm		30-60 cm		60-90 cm		Σ 0-90 cm				
Soil type (WRB, 2014)	Clay (Mean)	Cla (+/-)	Relative area	Absolute area	SOC stock	n	SOC stock	n	SOC stock	n	SOC stock				
	[%]	[%]	[%]	[ha]	[t ha ⁻¹]	[Mt*ha]	[-]	[t ha ⁻¹]	[Mt*ha]	[-]	[t ha ⁻¹]	[Mt*ha]			
Gleyic Podzol	2.9	1.0	36.3	72954	137	10.0	16	60	4.4	16	20	1.4	19	216	15.8
Gleysol	6.9	5.8	13.6	27333	120	3.3	6	27	0.7	9	22	0.6	10	169	4.6
Podzol (Neocambic)	3.7	1.4	12.4	24921	74	1.8	3	26	0.6	4	11	0.3	5	110	2.8
Cambisol/Brunic Arenosol	3.7	1.6	11.2	22509	86	1.9	7	21	0.5	12	10	0.2	14	117	2.6
Podzol	2.6	1.3	8	16078	66	1.1	8	28	0.5	13	10	0.2	17	104	1.7
Rheic Histosol	-	-	6.1	12259	311	3.8	5	214	2.6	10	158	1.9	12	684	8.4
Ombic Histosol	-	-	3.7	7436	242	1.8	3	179	1.3	6	162	1.2	6	582	4.3
Sum			91	183490	24		48		11	70		6	83		40
Others			9	17485											

Table 1 (Continue). Depth-specific soil organic carbon (SOC) stocks from 0 to 90 cm depth for the most frequent soil types with a relative area > 3 % in the different geological regions in Schleswig-Holstein. *n* = number of soil profiles.

Higher "Geest"					0-30 cm			30-60 cm			60-90 cm			Σ 0-90 cm		
Soil type (WRB, 2014)	Clay (Mean) [%]	Clay (+/-) [%]	Relative area [%]	Absolute area [ha]	SOC stock		<i>n</i>	SOC stock		<i>n</i>	SOC stock		<i>n</i>	SOC stock		
					[t ha ⁻¹]	[Mt*ha]	[-]	[t ha ⁻¹]	[Mt*ha]	[-]	[t ha ⁻¹]	[Mt*ha]	[-]	[t ha ⁻¹]	[Mt*ha]	
Cambisol/Brunic Arenosol	4.5	2.0	18.2	68535	79	5.4	33	19	1.3	34	8	0.5	35	106	7.3	
Stagnosol	15.5	8.8	11.9	44811	93	4.2	51	26	1.2	49	11	0.5	54	130	5.8	
Gleyic Podzol	3.7	1.4	10	37657	138	5.2	16	66	2.5	15	18	0.7	19	223	8.4	
Stagnic Cambisol/Arenosol (Stagnic)	6.1	2.4	8.8	33138	63	2.1	8	20	0.7	6	12	0.4	8	96	3.2	
Podzol (Neocambic)	4.5	1.9	8.7	32761	96	3.1	7	23	0.7	11	9	0.3	11	127	4.2	
Gleysol	9.2	5.6	6.7	25230	108	2.7	10	31	0.8	10	18	0.4	14	157	4.0	
Anthrosol ("Colluvic")	7.9	1.5	6.2	23347	65	1.5	4	31	0.7	4	14	0.3	3	111	2.6	
Rheic Histosol	-	-	4.8	18075	307	5.6	11	204	3.7	14	173	3.1	18	684	12.4	
Stagnic Podzol	7.3	2.6	4.7	17699	154	2.7	10	49	0.9	7	11	0.2	11	214	3.8	
Podzol	3.8	2.0	4.5	16945	97	1.6	24	37	0.6	24	14	0.2	27	148	2.5	
Plaggic Anthrosol	7.5	-	4.3	16192	92	1.5	1	65	1.1	1	21	0.3	1	178	2.9	
Luvisol	11.8	0.3	3.4	12803	61	0.8	2	23	0.3	2	11	0.1	2	94	1.2	
Sum			92	347193		36	177		14	177		7	203		58	
Others			8	29372												

Table 1 (Continue). Depth-specific soil organic carbon (SOC) stocks from 0 to 90 cm depth for the most frequent soil types with a relative area > 3 % in the different geological regions in Schleswig-Holstein. *n* = number of soil profiles.

Marshland

Soil type (WRB, 2014)	Clay (Mean) [%]	Cla (+/-) [%]	Relative area [%]	Absolute area [ha]	0-30 cm			30-60 cm			60-90 cm			Σ 0-90 cm		
					SOC stock [t ha ⁻¹]	SOC stock [Mt*ha]	<i>n</i> [-]	SOC stock [t ha ⁻¹]	SOC stock [Mt*ha]	<i>n</i> [-]	SOC stock [t ha ⁻¹]	SOC stock [Mt*ha]	<i>n</i> [-]	SOC stock [t ha ⁻¹]	SOC stock [Mt*ha]	<i>n</i> [-]
Eutric Fluvisol Gleysol (Drainic)	25.8	7.7	27.0	77048	69	5.3	20	32	2.4	40	23	1.8	43	124	9.5	
Fluvisol Gleysol (Drainic)	36.8	7.7	17.6	50224	70	3.5	19	38	1.9	39	31	1.5	45	138	7.0	
Calcic Fluvisol Gleysol (Drainic)	15.8	7.2	16.8	47941	51	2.5	36	25	1.2	47	20	0.9	50	96	4.6	
Fluvisol Gleysol (Clayic, Drainic)	42.5	8.6	8.2	23400	100	2.3	4	53	1.2	5	39	0.9	7	192	4.5	
Rheic Histosol	-	-	6.7	19119	259	5.0	1	223	4.3	2	192	3.7	2	674	12.9	
Calcic Fluvisol Gleysol (Salic)	18.6	11.0	4.5	12841	58	0.7	7	34	0.4	9	36	0.5	14	128	1.6	
Ombic Histosol	-	-	4.0	11415	285	3.3	6	177	2.0	6	230	2.6	5	692	7.9	
Fluvisol Thionic Gleysol (Hyperhumic)	37.5	16.5	3.0	8276	198	1.6	3	207	1.7	6	88	0.7	7	493	4.1	
Sum			88	250264		24	96		15	154		13	173		52	
Others			12	35100												

- Effect of SOC on soil structure formation and strength

The link between the SOC and clay content may allow one to indirectly define soil strength based on the clay mineral associations, expressed as the SOC:clay ratio. Because Illites dominate the clay fraction in Schleswig-Holstein, no further mineral specific interactions need to be considered.

Irrespective of soil management, a weak positive relationship between SOC and clay content arises first for soils containing > 12 % clay, indicating the lowest threshold at which clay-carbon-associations play an important role for SOC storage processes (Figure 4). The relationship becomes closer for soils with higher clay content, i.e., > 20 %. Based on this, SOC:clay ratios are calculated only for soils with a clay content > 12% and are differentiated for the three land use systems (Figure 5).

A management specific differentiation, however, results in the data, which also show the varying sensitivity of soils and sites. In particular, the forest sites have the greatest ratio followed by the grassland sites, while the arable soils have the smallest value in the top 30 cm depth. The SOC:clay ratios are also attributed to structure quality classes according to Johannes et al. (2016). The smaller the ratio the less structured is the soil. SOC:clay ratios vary from < 1:13 (only for arable sites) to over 1:10 (predominantly for grassland sites) to > 1:8 (predominantly for forest sites) (Figure 5).

An additional classification for soil structural quality (based on our own results) of the arable, grassland, and forest sites for the clay classes is as follows: > 12 % and > 20 % in good (> 1:8), medium (1:10 up to 1:8), bad (1:13 – 1:10) and insufficient (< 1:13) soil structural quality. These classifications show a detailed differentiation among the 3 management systems (Table 2).

Table 2. Classification of the structural strength expressed as SOC:clay ratio in dependence of the clay content > 12 % (a) and > 20 % (b) for the 3 main land use management systems: arable land, grassland and forest. The smaller the value of the SOC:clay ratio the less structured are the soils.

a) Clay content > 12 %				
Land use type	SOC:clay > 1:8	1:10 < SOC:clay < 1:8	1:13 < SOC:clay < 1:10	SOC:clay < 1:13
	[%]	[%]	[%]	[%]
Arable land (A)	10	14	16	60
Grassland (G)	37	15	14	34
Forest (F)	81	19	0	0
b) Clay content > 20 %				
Land use type	SOC:clay > 1:8	1:10 < SOC:clay < 1:8	1:13 < SOC:clay < 1:10	SOC:clay < 1:13
	[%]	[%]	[%]	[%]
Arable land (A)	8	10	8	73
Grassland (G)	21	19	14	47
Forest (F)	0	0	0	0

When focusing on coarser textured soils, the forest sites are mostly well-structured due to the higher SOC content in forest topsoils compared to those under arable or grassland management. However, arable soils in the top 30 cm are mostly insufficiently structured and

only 10 % are classified as good. Grassland soils have a medium position, as both very good, but also not appropriate, structural conditions can be found in them (Table 2a).

The results for the soils with clay contents > 20 % underline the higher sensitivity of arable soils and grassland sites for a worse structure (Table 2b). These soils become more sensitive to structure collapse, as can be seen from the increasing proportion of the sites with ratios < 1:13.

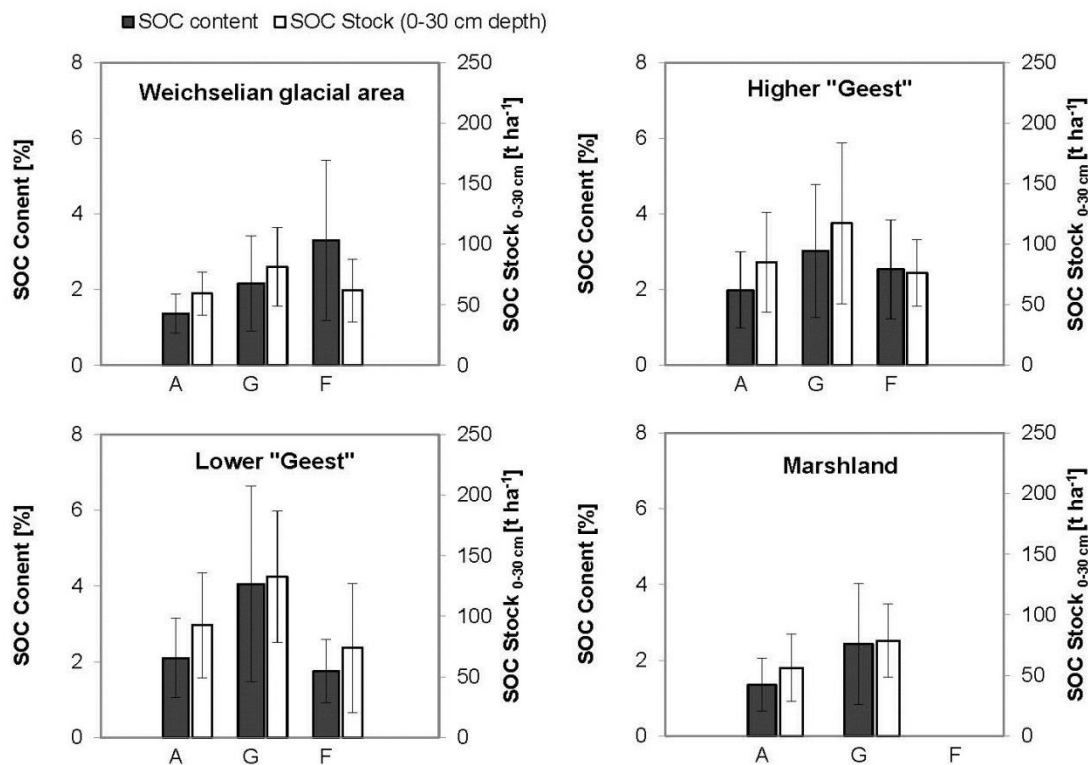


Figure 3. Effect of land use management (A = Arable land, G = Grassland, F = Forest) on mean soil organic carbon (SOC) content of mineral A-horizons and SOC stock within 0–30 cm depths for the region-specific soil types in Schleswig-Holstein. Representative soil types for each geological region and corresponding number of soil profiles are given in Table 1. Organic soils are excluded.

Discussion

Soil strength and soil functions depend on site-specific physical and chemical properties as well as on the biological activity, which can improve soil structure and soil functions but also worsen them. There are links among internal soil parameters, physical and chemical functions, and externally applied chemical, physical, and anthropogenic stresses.

They are responsible for soil degradation and may finally result in a reduced soil resilience, food production security, and groundwater recharge (Janzen, 2004). The enhanced sensitivity of soils due to soil slaking, erosion, reduced filtering, and buffering can be linked to soil structure strength changes and affected pore continuity (Gliński et al. 2011). Soil structure formation is, therefore, of main importance for soil processes all over the world and requires special attention. Aggregate formation always starts from coherent structure with

swell-shrink and shear induced formation of prisms, blocky, and subangular blocky structure. Biological activity, as well as physicochemical processes, often additionally strengthens the formed aggregates (Blume et al., 2016). In this context, the formation of organo-mineral-bondings is of central importance, as the rigidity of these linkages between soil particles and organic components is well proven (Six et al., 2002), and may also prevent enhanced swelling because of hydrophobic coatings on the particle surfaces coinciding with a reduced accessibility for water.

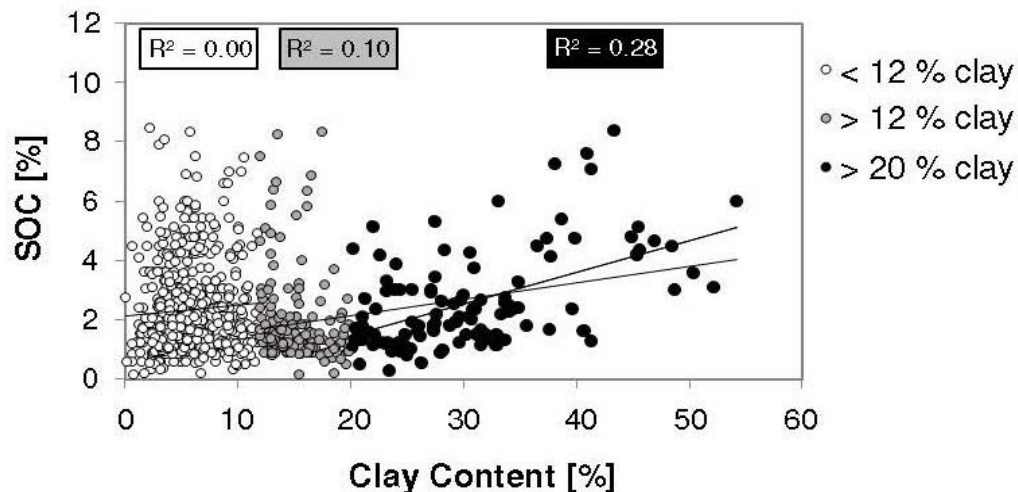


Figure 4. Relation between soil organic carbon (SOC) and clay content for mineral A-horizons for the clay content classes: 0 – 12 % (“< 12 % clay”), 12 – 60 % (“> 12% clay”), 20 – 60 % (“> 20 % clay”) ($n = 807$).

Obalum et al. (2017) state that, rather than the temporal change and potential amount of SOM, the absolute amount is most important when evaluating soil degradation. Lal (2018) stated that based on various further publications, the global magnitude (Pg) of soil organic carbon (SOC) is 677 to 0.3 m, 993 to 0.5 m, and 1,505 to 1 m depth. Thus, ~55% of SOC to 1 m lies below 0.3 m depth. Soils of agroecosystems are depleted of their SOC stock and have a low use efficiency of inputs of agronomic yield. He furthermore states that the temporal change in global land use since pre-agricultural understanding natural ecosystems to 2015 can be related to changes in land management because the land areas under croplands and pasturelands have increased while that under forest, savanna, and shrubland have decreased.

This, however, causes a dilemma, because sufficient detailed datasets, either for large areas or for small areas, are only seldom available which also makes the comparison and the quantification of scenarios difficult. If soil type specific variations at the state level in Germany are included, the actually calculated SOC stock in Schleswig Holstein is slightly higher than those in the state Saxonia Anhalt but slightly smaller in Baden Württemberg (LAGB, 2014; Waldmann and Weinzierl, 2014). The latter has a greater area. The main reasons for such differences are the presence of peat and marsh soils because marsh soils contain already initially a certain SOC stock as parent material. Wiesmeier et al. (2012, 2013) prepared datasets and maps for Bavaria based on nearly 1500 soil profile datasets. They concluded that in general grassland soils stored the highest amount of SOC down to 1 m, with a median value of 11.8 kg/m^2 , whereas considerably lower stocks of 9.8 and 9.0 kg/m^2 were

found for forest and cropland soils, respectively. These data are in an identical range as the presented data for Schleswig-Holstein, if we consider the whole soil profiles down to 90 cm (compared to 1 m in Wiesmeier et al., 2012). Most of the SOC stocks are stored in the topsoils, irrespective of the management type. If we also include the ploughing effects on the deeper distribution of SOC in the whole profile, our datasets and calculations are also in agreement with those for Bavaria. The deeper ploughing may be one of the main reasons for the 25 % organic carbon in 30 – 60 cm depth. Due to the anthropogenically enhanced soil changes with time, „Colluvic“ Anthrosols and Plaggic Podzols (or colluvic, plaggic material) show a higher SOC stock and a more even distribution, while in the sandy outwash area (lower “Geest”) only the Gleysols with a higher proportion of histic properties show high values.

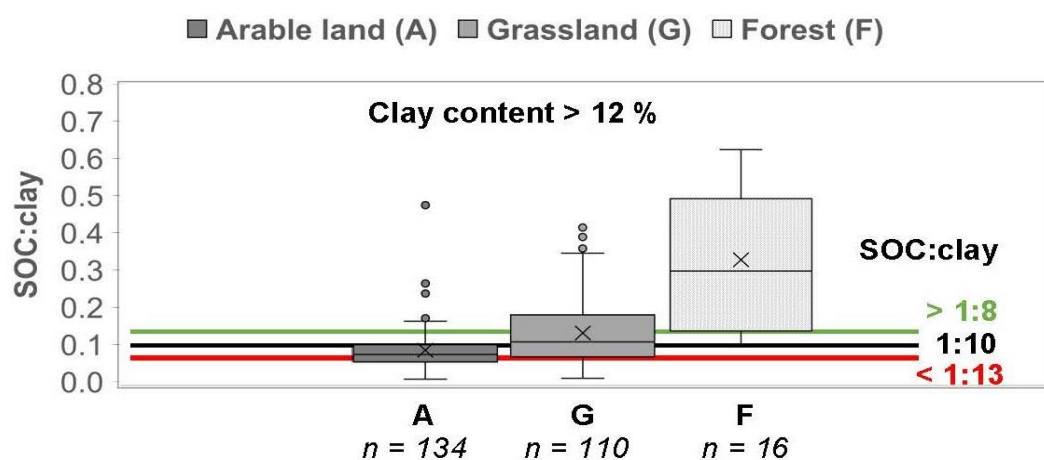


Figure 5. Effect of land use management system on the soil organic carbon (SOC):clay ratio for the A- horizons of soils with clay contents > 12 % in the four representative geological regions of Schleswig-Holstein. The smaller the ratio the less structured are the soils.

The ratio between SOC and clay content has often been mentioned in connection with the application of SOC stock datasets for the quantification of soil structure strength. Dexter et al. (2008) as well as Czyz et al. (2017) discussed the ratio between these parameters and concluded that, on average, the ratio should be about 1:10 in order to provide a sufficient coverage of the mineral surfaces with organic material to provide strong bondings among the particles. Johannes et al. (2017) furthermore differentiated the classification in order to get a better insight into soil physical and environmental processes. According to their findings, they concluded that, the smaller the ratio, the worse are the structural strength conditions. Comparing our results with their findings, we must conclude that the arable soils in Schleswig Holstein have a less favorable structure than the grassland and the forest sites in the top 30 cm; the latter ones seem to have the most favorable structural strength conditions based on this approach. Higher clay contents coincide with decreased SOC:clay ratios (<1:13) representing an insufficient soil structural quality, and define these soils as more sensitive to soil deformation. In particular, arable soils are throughout the year exposed to repeated wheeling and tillage operations even under less favorable soil moisture conditions.

Consequently, these soils are more intensely sheared and kneaded than grassland and forest soils, which cause an increased sensitivity to soil deformation (Hartge and Horn, 2016).

However, grassland sites with less stress application throughout the year are not only stronger aggregated but also have a better linkage between the clay and organic carbon components and are, therefore, less susceptible to soil deformation. The conversion of arable into grassland soils, therefore, helps to gain more strength even if such changes take a long time. Ajayi and Horn (2016) showed these strength increases with time in stagnic Luvisols and Cambisols; but, even nearly 20 years after the conversion, there was still an ongoing strength gaining process.

How far these correlations define increases in strength must, however, be discussed in view of the composition of the organic carbon pool (Stockmann et al., 2013). Wiesmeier et al. (2014) stated that for the Bavarian soils around 90 % of total SOC stocks can be assigned to the intermediate and passive SOC pool in cropland and grassland soils. They also stated that high SOC stocks in grassland soils would be partly related to a higher degree of soil aggregation compared to cropland soils, and that forest soils were characterized by distinctly lower proportions of intermediate and passive SOC and a high amount of active SOC in form of litter and particulate organic matter. Thus, not only the total SOC amount but also its composition is relevant for the regaining of strength or its preservation. However, such information is not available for our soil profiles, although it would certainly help to further elucidate the interactions among aggregate formation, changes in accessible particle surfaces, and the coinciding strength changes. Also, we have not yet described the in situ soil conditions, because the detailed, high-tech conditions for the analysis would require undisturbed, i.e., structured, soil samples, which are impossible to obtain at the present time. Kögel-Knabner and Amelung (2013) described the interactions between mineral and organic components and pointed out that analyses of them would be feasible in order to get detailed information concerning the composition on various scales. But there are still many unsolved questions. One of the major open topics is the scale dependency and the necessity to extrapolate strength conditions from the small to the landscape scale. Babel et al. (1995) defined the interactions of mineral particle arrangements and organic matter amount on the functioning of aggregates at various scales. They also stated that surface accessibility and availability need to be linked to physicochemical processes, in view of the question of how far we can define the SOM properties and amount in structured soils, in order to predict sustainable soil properties and functions on all scales.

Conclusion

SOC stocks in Schleswig-Holstein differ depending on the land use management system and the clay content of the soil type.

Arable soils are most sensitive to soil deformation, and the higher the clay content is the less rigid they are, if the SOC:clay ratio is used as an index.

Grassland topsoils showed the highest SOC stocks and a mediate structural quality. The latter was highest for forest soils, which, however, have a higher SOC content, but, at the same time, less fertile SOC composition (litter with high C: N ratio).

Further research on the carbon composition (labile, active, intermediate, or passive pools) would help to get a better insight into the role of SOC on soil strength and soil functions.

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Some Aspects of Bio-Environmental Problems and Further Development of Science and Scientific Policy in European Countries.

Ognyan Stoyanov Kostov*, Oswald Van Cleemput**

*Nexus Technology Consultancy, Research Advisor, Bulgaria

**Ghent University, Belgium

Corresponding Author: Ognyan Stoyanov Kostov, e-mail: ognyan.kostov@gmail.com

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Abstract

There is a lot of concern about climate change, nature and quality of life of people. Human activities directly affect more than 70% of the global ice-free land surface. Land also plays an important role on climate. Sustainable land and forest management can prevent and reduce land degradation, maintain soil fertility and productivity and reverse the adverse impact of climate change and land degradation. The present state of our environment, problems and future for EC science and science policy are presented in this paper. The actual status with regard to agriculture, industry, food, environmental microbiology, production and consumption of greenhouse gasses and how microorganisms will be affected by climate change and how microorganisms affect climate changes and other human activities are shown. Quality of life and suitability of environmental policies are discussed. Analyzes, contribution and problems of environmental policy are demonstrated. Future purposes, priority areas and directions of the environmental EU policy are also presented. In addition, policies for implementation of bio-environmental strategy as complex purpose are discussed. Supporting of scientific persons involved in this policy, enough financing of environmental sciences and identifying priority areas were shown. Financial regulation for environmental policy and priority areas are being underlined. The following aspects are also handled: protection of intellectual property, science infrastructure, government and private science units, updated supply of science policy information, as well as cooperation and coordination between EC members. Building scientific centers to study the relationship among environmental science and policy and business are presented. Actions for implementation of the environmental strategy are recommended. More and more stronger standards for protection and maintenance of environmental quality are recommended. The EU countries have to initiate the introduction of new laws for protection of humanity and environment. The discussion of the above-mentioned problems strongly supports the paper: “scientist’ warning to humanity: microorganisms and climate change”. Some scientists predict environmental collapses at different periods. Bio, organic low impute and sustainable agricultural practices reduce the negative tendencies for natural processes, soil fertility, rate of contamination of soils, waters and air and climate changes. Poverty, soil contamination, ways of soil exploitation, low rate of waste management, rate of concern of nature by political leaders and governments have influenced the rate of climate changes. Better and stricter standards are needed for protection and maintenance of our environment. The EU countries can take an initiative for new laws to protect humanity and maintain our environment at the present level.

Key words: climate change, microorganisms, environment, scientific policy, soil, worming effect

Introduction

Environmental research and policy on the environment and natural resources that are fast depleting is due to overexploitation and to the anthropogenic activities. This will help people to find various ways and methods to maintain ecological balance, which our existence depends. Environmental research and policy plays a very important role in the conservation of the environment. In the past this problems were not enough clear and were underestimated. This was shown in our investigations (Kostov, O. (1973); Kostov, O. (1975); Kostov, O. (1976); Badjov, K. & Kostov, O. (1977); Kostov, O. (1977); Kostov, O. (1980). It was consider that nitrogen gasses were formed from agricultural fertilizers and have agronomical value but it was not predicted that investigated gasses such as NH_3 , NO_2 , N_2O and CO_2 will have such worming effect on the planet. In our experiments for reduction of N_2O to N_2 from 4 selected denitrifying strains only one, *Micrococcus denitrificans*, was able to reduced fully N_2O to N_2 for 7 days. It was promising result in laboratory conditions but difficult for execution in field conditions. Soil scientists were discussing mainly for agricultural value of N lost but not for environmental value. The figures shown in Figure 1, 2, 3 clearly indicated that humanity have to decide to take worming effect of the planet as first aim. Worming capacity of the oceans went up by 0.5-0.7°C but land temperature already have increased by 2°C (Figure 3). Agriculture, Forestry, and other land use activities accounted for around 13% CO_2 , 44% of methane (CH_4), and 82% of nitrous oxide (N_2O). (IPCC, Approved draft, 2019). Bringing more attention towards various environmental issue such as pollution, flooding's, droughts, higher temperatures, fast depletion of natural resources, low efficiency of environmental technologies, climate changes and worming effect will support scientists to find ways and methods to solve already existing environmental issues (Ricardo Caviceholi, Viliam J. Ripple Kenneth N., Nicole S. Webster etc. (2019); Yunusa Hassan and Lazarus Abore Embaye (2018); Figures 1, 2 and 3).

SOME OF THE MAIN OBJECTIVES OF EC SCIENCE POLICY

I. Creating strong support medium for better Environmental policy

The last 50 years world economy was increased about by 14 times causing massive increase in demand for energy and natural resources. The main purpose promises that for the next new 5 years period it will be approved so called "Green Agreement to 2050", which will change the following main activities of the European Government: 1. To convert basically priorities of EC for protection of Environment and reduction of climate changes and negative effect of them. 2. It will be done "green agreement" among EC members with only purpose to 2050 Europe to be environmentally neutral continent. It was concluded that purpose to reduce emission of CO_2 by 40% to 2030 is not high enough. The aim have to be much higher and emissions to be reduced by 50-55%. To support this purpose EC have to develop new laws called Climate laws. This activity needs new very high scale investments but public financial support will not be enough. New Sustainable European Investing Plan has to be created and parts of the European Investing Bank have to be changed to Climate Bank. This will open about 1 trillion EUR investment's in the next 10 years. In addition, Europe have to strengthen

their small and middle enterprises. All these things will release ability of many companies from all countries to have access for collecting financial supports. Together with these actions, the Agreement for sustainable development of EC will be improved. Consumers can also do their bit as well: by flying less and eating less meat. Governmental decisions and industry have to be watch more carefully to keep correct way for environmental protection directions. Large multinational bank associations have to be strongly involved in the environmental protection policy. In addition, a fundamental change of our market economy is required. About 130 countries that participate in Intergovernmental Science-Policy Platform on Biodiversity and Ecosystem Services (IPBES) already have endorsed IPBES report.

II. Importance of Environment for life: Soil, Water and Air

The basic components of the Nature which support life in the planet are: soil, water and air. Unfortunately almost half of our ecosystems have been severely damaged by agriculture, fishing, mining, climatic changes such as droughts, flooding's and many forest fires, disasters, entertainment activities and pollution. Soil, water and air are important medium for growth of plants and animals supply, foods for people and health of the people; and (2) They are also responsible for turnover rate of the main life important elements in the Nature (N mineralization, N₂ fixation, turnover rate of N, phosphorus transformations, micronutrients, water maintenance and supply for plants, maintenance humidity in air and supply drinking water for human beings, provide charcoals for production of electricity, responsible for purification processes in soil and reduction of N₂O produced from mineral fertilizers to N₂, maintenance of microbial diversity, insects, small and big animals and finally maintain all biodiversity. Soil, water and air support also development of plants, giving food for human beings, consumed accumulated CO₂ in the atmosphere and maintain acceptable temperature for life of the people. Air supply oxygen to all living organisms and water is the main component of all bodies of living organisms in the planet.

Unfortunately, in industrial areas of cities the air is very often contaminated with dust, heavy metals and makes direct infections to people. Soils are contaminated with heavy metals and chemicals. Usually this happen nearby metallurgic plants. It is strongly recommended air to be clean by artificial or raining clear water; soils have to be bio remediated from heavy metals and chemicals. In case these areas have composting plants they needed inhalation and purification though bio filters. Asthmas, heavy breathings, lung infections allergic reactions are very often cases in this areas. Usually this happen nearby metallurgic combines and smoke is falling nearby areas. It is strongly recommended air to be cleaned by artificial reining's with clear water, soils have to be bio remediated from heavy metals and pesticides, and if they have composting plants they needed inhalation though bio filters for the whole air coming from composting plants. Also significant contamination can be observed around mining activities for gold, copper, zinc and other precious elements. Air, soil and water are contaminated and need bioremediation of soils, air and waters.

There are publications which showed that if we live like Nature we need 2.7 planets (www.footprintcalculator.org). Mankind already used resources of the planet for this year 2 months earlier as compare with 20 years ago (Ricardo Caviceholi, Viliam J. Ripple Kenneth N., Nicole S. Webster (2019). This showed that there iare slow regeneration ability of the ecosystems. On July 29, humanity will have used nature's resource budget for the entire year according to Global Footprint Network (an international sustainability

organization that has pioneered the Ecological Footprint). Earth overshoot day falling on July 29th means that humanity is current using nature 1.75 times faster than our planet ecosystems can regenerate (www.footprintcalculator.org). The costs of this global ecological overspending are becoming increasingly evident in the form of deforestation, soil erosion, biodiversity loss, or the buildup the CO₂ in the atmosphere. Significant opportunities of this problem can be found in 5 key areas: cities, energy, food, population, and planet. For instance, cutting CO₂ emission from fossil fuel burning by 50% would move the Date by 93 days. Therefore, as many people as possible are involved in CO₂ reduction, the higher regeneration rate will be increased globally. For now 2.5 million users per year of American are now available in eight languages and with Chinese and Portuguese most recently added (<https://www.footprintnetwork.org> (2019); Global Footprint Network; “Advancing the Science of Sustainability”; <https://www.footprintcalculator.org/>, Oakland, CA, USA, July 23, 2019).

It is estimated that from 10% to 20% of the 450 billion tons of carbon emitted (Fig. 1) since the Industrial revolution may be attributed to soil carbon losses. Carbon that is released from the soil as CO₂ can traps heat and contribute to warming temperatures. Recent pooling in the USA shows 72% of American consider climate change an important issue, and 48% say that the science on climate change is more convincing than five years ago - mostly because they have seen evidence of more extreme weather. (Climate change, 2019). The results of this tendency is the restlessness, soil erosion, reduction of biological diversity and CO₂ in atmosphere. Some countries “burned” their limit faster like Kathar and Luxemburg (for 50 days from the beginning of the year) other like USA, Canada and Australia have option to 31 March. Cuba, Iraq and Ecuador are only countries, which can meet their limit to the end of the each year. It is important to note that together with exhausting of natural resources, the increase of poverty in population was observed. Scientists, practitioners, and stakeholders will be invited to document this topic and to present solution for pro-poor and gender sensitive strategies with objectives to improve human and environmental well-being at the same time. From the Figure 1 it can be seen that the most CO₂, as warming equivalent, is at the part of CO₂ from fossil fuels - 62%; from methane (CH₄)- 16%; from nitrous oxide, (N₂O) - 6%; CO₂ chemicals - 3%; F-gas - 2% and from Eyaz. All gasses are important and can be reduced as much as possible by conditions and circumstances. Fossil fuels as biggest proportion can be tried to be replaced by substituting energy from them by using nature sources such as water, electricity from water, wind, atomic centrals for electricity, biogas plants which consume CO₂ to produce methane which is burn for electricity etc.

III. Environmental activities

1. Agriculture

Types of agricultures can be bio, organic, mixed bio-organic, using only mineral fertilizers, low impute, sustainable, high impute, exporting and etc. According to World Bank (World Bank data on agriculture) nearly 40% of the terrestrial environment is devoted to agriculture. This proportion is predicted to increase, leading to substantial changes in CO₂ and N₂O production and soil cycling of carbon, nitrogen and phosphorous among other nutrients. Furthermore these changes are associated with market loss of biodiversity including soil microorganisms. Methanogens produce methane in natural and artificial anaerobic

environments (sediments, water saturated soils such as paddy soils), waste waters, biogas facilities etc. and denitrifying bacteria produce N_2O in all soils, waste alters and sediments produced CO_2 . For reduction of this negative influence the following measures can be taken: improving structure of agriculture, cities, forests reserved, areas regrading significant reduction of global warming, climate changes and balance of used ecosystems. Extended research and analyses on better soils distribution for usage can be: a). high fertility soils with sustainable yields; b). medium fertility soils with sustainable yields; c). low fertility soils. Important are means and ways to use; extended of regeneration agriculture; improve their fertility by: pH corrections, microbial diversity, crops suitability and crops rotations, reduction of NO_3-N doses to decrease N_2O formation at the same level of yield. (Kostov, 1973, 1975, 1976, 1977, 1980). Significantly to be increased areas of N_2 -fixing crops with wide usage of microbial fertilizers for higher symbiotically N_2 -fixation (Kostov and Lynch, 1997). In this way legume grasses can play an important role for supporting animal breeding thus supplying animals with cheaper food to fight poverty. In addition, to increase oil producing crops (vineyards, rape (seeds), olive oil plants etc.) to increase value added thus to contribute to the circular economy. It has to be improved the study of effect of present practices of agriculture on environmental contamination regarding soil, air, water and waste management. It has to be improved research policy to reduce plant diseases and encourage all types of biological agriculture (legumes areas, legume forage crops, organic agriculture, manure and compost formation and application, biochar production and making new combined bio organic fertilizers such as “compost + biochar + *Trichoderma harzianum* (bio control agent)”. Rice feeds half of the global population and rice paddies contribute 20% of agricultural CH_4 emissions despite covering only 10% of arable land. Anthropogenic climate change is predicted to double CH_4 emissions from rice production by the end of the century. It has to be done new calculations which have to include consumption of CO_2 in all biogas plants during process of methane formation in the world by using formula: 1 molecule of CO_2 produce 1 molecule CH_4 at -120 mV oxy- reduction potential. It must have immediate reactions for all new Environmental technologies suggested in the world. (European Commission, Brussels,(2016), COM (2016) 157 final).

2. Nature risks, microorganisms and climate change

Human activity and their effect on the climate change and environment cause unprecedented animal and plant extinction, cause loss of biodiversity and endanger animal and plant life on Earth (Ricardo Cavicchioli etc., 2019). In the Anthropocene, in which we now live, climate change is influencing most life in the Earth. Microorganisms support the existence of all higher trophic forms. Climate changes also affects microorganisms (Kostov, O., J. Lynch & L. Elliott, (2002). Climate influence the structure and diversity of microbial communities directly (seasonally and by temperature and moisture content) or indirectly by plants composition, plant litter and root exudates. Soil microbial biodiversity influences plant diversity and its importance of ecosystem function, including carbon cycling. Elevated CO_2 concentrations enhance competition for nitrogen between plants and microorganisms. Thus, climate changes resulted in overall alterations to global nitrogen and carbon cycle that reduce terrestrial carbon sequestration. Although microorganisms are crucial in regulating climate change, they are really the focus of climatic change studies and they are not enough considered in policy development. Their immense diversity and varied responses to

environmental changes make determining their role in the ecosystem challenging. It is time to illustrate the links between microorganisms, macroscopic organisms and climate change, and put humanity on notice that the microscopic majority can no longer be the unseen elephant in the space: emit affect climate change and climate change affect microorganisms: ocean warming and acidification, acidification of soil, eutrophication, overuse (fishing, tourism, shifts microalgae, disappearance of coral). Autotrophic respiration by plants (60 Pg. C per year) and heterotrophic respiration by microorganisms (60 Pg. C per year) release CO₂ back into atmosphere. Warming is expected to accelerate carbon release into the atmosphere. Forest cover 30% of the land surface, contain 45% of terrestrial carbon, make up 50% of terrestrial primary production and sequester up to 25% of anthropogenic CO₂. Graceland cover 29% of terrestrial surface. Non-forest, arid and semiarid regions (47%) are important for the carbon budget and respond differently to anthropogenic climate change then forest regions. Lake Make up 4% from the non-glaciated land area and shallow lakes emit substantial amount of CH₄. Peat covers 3% of the land surface and as global carbon sink contain 30% of soil carbon. The fire in Russia showed another role of peat. It can be burned and maintain fire in North Russia areas now. Climate warming changed 1.5-2°C organic matter into biomass, microbial respiration and greenhouse gas emissions.

Higher CO₂ levels increase primary productivity which resulted in higher carbon emission due to the microbial degradation. Plants release 50% of fixed carbon into soil which is available for microbial growth but they also release CO₂ in atmosphere. Soil microorganisms also produce N₂O which is much more dangerous for global warming (Ricardo Caviceholi, Viliam J. Ripple Kenneth N., Nicole S. Webster, 2019). Climate changes affect microbial diversity directly and indirectly. Soil microbial diversity influence plant diversity and is important for ecosystem function, including carbon cycle. Climate changes directly and indirectly influences microbial communities and their functions through several factors such as temperature, precipitation, soil properties, and plant root exudates. Tundra microbial communities change in the soil layer within 1.5 years of warming, the functional potential of microbial communities changed markedly, with an increasing amount of genes involved in aerobic and anaerobic carbon decomposition and nutrient cycle. Rapid warming in Antarctic Peninsula is also a problem. Climate changes are likely to increase the frequency, intensity and duration of cyanobacterial blooms in many eutrophic lakes, reservoirs and estuaries.

Climate changes affect microorganisms. Microorganisms also can affect climate changes. In our experiments (1973-1976) not all denitrifying bacteria were able to reduce N₂O to N₂ (Badjov K. and Kostov O. 1977). From 4 selected strains only one (*Micrococcus denitrificans*) was able to reduce fully N₂O to N₂ for 7 days thus positively influenced climate changes. Increasing the temperature and droughts strongly affect ability of plants to grow (Vasileva and Kostov, 1998). Climate change affect different soil bacteria and soil fungi. The fungal population is more resistant to dry conditions. The reduced soil microbial activity reduces the overall functional potential of communities, and thereby limiting their capacity to support plant growth. Climate change affect the occurrence and spread of diseases in marine and terrestrial biota. For example there is a strong link between increasing of sea surface temperature and coral diseases. Anthropogenic climate change stresses native life, thereby enabling pathogens to increasingly cause diseases. Human activities, such as population

growth and transport, combined with climate change increase antibiotic resistance of pathogens and the spread of waterborne and vector borne pathogens. Therefore increasing of diseases of humans, other animals and plants. Population growths, which amplify climate change, is also an important factor in contributing to the development of resistance.

As a result microorganisms make a major contribution to carbon sequestration, particularly marine phytoplankton, which fix as much as CO_2 as terrestrial plants. Microorganisms also contribute substantially to greenhouse gas emissions via heterotrophic respiration (CO_2), methanogens (CH_4) and denitrification (N_2O) (Badjov K. and Kostov O., 1977). Human activity that directly affects microorganisms includes greenhouse gas emissions, (particularly CO_2 , CH_4 and N_2O), pollution (particularly eutrophication, agriculture (particularly land use), and population growth which positively feedback on climatic change, pollution, agricultural practice and the spread of diseases (Vasileva, V. & Kostov, O., 2002). Human activity also can accelerate climate change. By contrast, microorganism also offered important opportunities for remedying human cause problems through improved agricultural practice and outcomes, production of biofuels, production of biofertilizers for legumes and remediation of pollution. Addressing specific issues involving microorganisms will require targeting laboratories. These labs activities should be followed by field tests. We must improve our quantity understanding of the global marine and soil microbial functions related to the environmental suitabilities.

In this consensus, statement that it is illustrated the link between microorganisms, macroscopic organisms and climate change, and put humanity on notice that the microscopic majority cannot longer be the unseen, and put humanity in environmental risk. We have to appreciate the importance of microbial processes and it will be fundamentally our understanding of the Earth's biosphere and response to climate change (Ricardo Caviicchioli, William J. Ripples etc., 2019).

Heavy metals contamination of soils is very serious factor for soil fertility, soil respiration and soil microorganisms number, functions and ratios. In addition, contamination of soils with heavy metals significant reduce functional diversity and biodiversity of soil microorganisms. More information for Cu toxicity to soils and soil microorganisms are reported by Kostov O., O. Van Cleemput, 1997; Kostov O., O. Van Cleemput, 1998; Kostov, O., O. Van Cleemput, 2001; Kaloyanova N., Petkova N., Kostov O., 2009; Kostov O., O. Van Cleemput, 2012a; Kostov O., T. Ngan, 2002b); Kostov O., 1997, Kostov, O., Lynch, J. M. (1998). Generally bacteria and symbiotic N_2 -fixing bacteria were more sensitive to copper contamination as compare to fungal and actinomicetes populations. Affected microorganisms showed higher specific respiration rate ($\text{C-CO}_2/\text{biomass C}$). They release more CO_2 in air for their surviving in toxic conditions. Bioremediation of toxic amount of Cu can be successful by application to soil of correct amount of well-matured compost rich in normal microorganisms and their ratios of bacteria/actinomicetes/fungi and this have to be combined with correct amount of lime for correction of pH to neutral value of 7.0. Duration of contamination also have negative importance. Microorganisms which are is stress conditions from Cu toxicity need more energy for surviving but possibility of soil to support surviving is less and therefore the rate of stress is increasing corresponding to the time under heavy metal stress (Ross, S., J. Kaye (1994). One way to recover soil fertility and it functions is application of well-matured compost enriched with useful soil microorganisms with high

metabolic rate and ability to survive in stress conditions. These composts are inoculated and contained microorganisms such as selected strains of *Trichoderma harzianum* with association with very good N₂-fixers. Strains from genera *Azospirillum*, *Azotobacter* spp are better N₂ fixers but they have low ability to survive in contaminated conditions (Kostov, O. & Lynch, J. M. (1998). Duration of copper contamination also have ecological importance. It was established in Bulgarian soils that Cu contamination is stronger when duration of Cu contamination lasted more then 6 months and the rate of contamination is more then 5% (Kostov, O., 1997), (European Commission, Brussels,(2016), COM (2016) 157 final). Climate change, including increases in frequency and intensity of extremes, has adversely impacted food security and terrestrial ecosystems as well as contributed to desertification and land degradation in many regions (IPCC, 2019). Climate change create additional stresses on land, exacerbating existing risks livelihoods, biodiversity, human and ecosystem health, infrastructure, and food systems. Increasing impacts on land are projected under all future GHG emission scenarios. Some regions will face higher risks, while some regions will face risks previously not anticipated (IPCC, 2019). The level of risk posed by climate change depend both on the level of warming and on soil moisture content, how population, consumption, production, technological development, and land management practice are used. Approaches with higher demand for food, feed, water, higher resource consumption and production, and lower technological developments and improvements in agriculture yields will resulted in higher risks from water deficiency in dryland, land degradation and food insecurity (IPCC, 2019).

IV. Environment policy: measures, assessment, recommendations

Policies related to the food system, reduce food and waste lost, people and environment will better accept support more sustainable land use management, enhanced food security and low emissions. Such polices can contribute to climate change adaptation and mitigation, reduce land degradation, desertification, poverty and improved people's health (IPCC, 2019). Policies related with more manners that are flexible, can maximize benefits and minimize risks for land management decisions from farm level to national scale (IPCC, 2019). This type of policy have to support increasing of biogas plants using waste waters from towns and villages to delivery energy (methane) and consume CO₂; In addition, it will be strongly useful creating new technologies for less waste discharged by recognizing problems, science prognoses for maintenance of high yields and protection of ecosystem (soil - water - air). It is needed better scientifically assessment of existing environmental situation. Peoples need new methods and equipment's for measuring environmental indicators and protection. It is obviously that financial support have to be increase for Nature protection every year and 4 years ahead; Organizing new specializes scientific laboratories and industries are also needed; It have to be improved interaction by policy makers, scientists and politicians among EU countries for better future of EU countries. This will be very important to do planning of science policy to meet higher requirements of EU farmers and population. The Science Policy should initiate legislative processes in EU members to support decrease of global warming and decrease contamination of soil, air, waters and reduction amount of wastes. In addition it has to be increased effectiveness of communication between Science Policy Office Bureau/ EU members/ and EU media and environment business man. Science policy have to be better orientated to increase publications activity by writing blogs, journal articles,

newspaper articles, using LinkedIn and Facebook Portals and giving more presentations with higher standards in ordinary media. It will be better to increase the trust of EC members to the Central EC management science policy; The Science Policy has to support development of new approaches and methods to assess and give legislative support of EC environment policy on the field of climatic changes, biodiversity, soils fertility and water resources; It has to be encourage making scientifically proposals on the field of environmental problems. The Science Policy need to formulate more clearly science policy and strategy of EC countries; It have to increase efficiency of European Science policy by promoting activities and influence decision-making in the relevant fields; The Science Policy have to make attempts to improve better collaboration, coordination, information, with EC members and potential partners on the field of priority areas of soil, water, air and wastes; It has to publish the present EC positions regularly including in many media and all in line of management and communication units; It has to support financing of research on selection of partners of bacteria/N₂ fixing plants relationship such as soybean, Lucerne, peas, groundnut etc. thus to achieve 30% reduction of N₂O released into atmosphere from NO₃ containing mineral fertilizers applied. Depending on specific country it has to be supported specified research on N₂O releasing from soils by microbiological and biotechnological point of view. Complex assessment is needed to assess environment related to productive value of ecosystems and it have to be evaluated taking into account all parameters such as metric, energetic, social, human health and compare at beginning of the same nature parameters. Waste management is important for climate change and has to be done the following activities: 1. Using town wastes, regenerate disturbed lands and create new soils, significant increase production of green biomass for CO₂ consumption, O₂ production and aerobic advance composting of all wastes. 2. Management of plastic wastes (they are chemically and physically neutral): to carry out experiments for composting and followed by introduction to soils for physical properties improvements. It has to start mass growing green plants in towns, roads, mountains etc. for consumptions of CO₂ in EC and in the world. The Consensus Statement warning to humanity underline perspective of microbiology to regulate climate changes. It will raise awareness of the microbial word and will make a call to action to microbiologists to become increasingly engaged in and for microbial researches to become increasingly integrated into the framework for addressing climate change and accomplishing the United Nation Sustainable Development Goals (Ricardo Cavvicchioli and etc. ORCID, 2019); Zero waste discharged bio technologies have to be supported, financially encouraged and internationally awarded for better stimulations and protection of environment. (European Commission, Brussels,(2016), COM (2016) 157 final). These type of polices include individual and institutional level, accelerate knowledge transfer, enhance technology transfer, enable financial mechanisms, implement early warning systems, undertake risk management and address gaps in implementation and upscaling (IPCC, 2019). These type of policies will address climate change adaptation, mitigation, desertification, protect land degradation and food security, and can bring social and ecological economic and will contribute to poverty eradication. Delaying climate mitigation and responses across sectors would lead to increasingly negative impact on land and reduce prospects of sustainable development (IPCC, 2019). The effectiveness of decision-making and governance can be enhanced by the involvement of local stakeholders: particularly those most vulnerable to climate change including indigenous people and local

communities, women, and the poor and marginalized in the selection, evaluation, and implementation and monitoring of policy instruments for land-based climatic change adaptation and mitigation. Integration across sectors and scales increase the chance of maximizing co-benefits and minimize tradeoffs (IPCC, 2019).

V. Building measures for applications and protection means:

Start building of small scale units for production of bio fertilizers, microbially produced enzymes, inoculated composts and purification of waters and air.

A. Maintaining of policy for adapting to EC conditions production of all available bio fertilizers and enzymes having in mind definite country, soil types and crops conditions and sustainable production and protection of environment. It is needed financial support to all existing microbial culture collections of EU members;

B. It has to be started using virgin lands, re-cultivation of destroyed soils from mining and road building industry in towns and, bioremediation of heavy metals contaminated soils; It is necessary to increase using in all cities green wastes for biogas production and composting. More advanced methods have to be used for increasing efficiency of purification of town waters using microbiologically produced enzymes cellulase,s and lipase,s. etc. (European Commission, Brussels, (2016), COM (2016) 157 final)

VI. Administrative and other policies applications for discussion

To support research policy for production of healthy food we need bio organic policy including for bio pesticides, not using genetically modified organisms and using only useful microorganisms. More efficient work and control of EC Environment Ministers, Environment Agencies and Commissions to support and increase number and production ability of environment protection units in all EC countries. To find suitable support to those farmers, which do not required high profit from yields production but express high care for environment protection. More support needed for bio farmers to increase number of these farmers and for better protection environment areas. The higher level needed for adapting policy for extra incomes of EC countries which have to be directed to bio farmers. All extra income have to be directed from Council of Ministers in each country to avoid corruption and directed to the Ministry of Agriculture. To increase number of visits as much as possible to all scientific and environment exhibitions in the world. It is needed to expressed and showed better science policy and care, for protection of soils from disasters such as seasonal dryings, droughts, flooding's, increasing areas of drop way of irrigation, air contamination from metallurgic enterprises, applying regeneration methods in very low yielding soils, introduce environment (ecological) stamp to as many as possible farmers in EC, to introduce new higher yielding cultivars and in the same time to use less mineral fertilizers (higher efficient photosynthesis), to make history record of environment protection, more usage of organic and bio fertilizers production units etc. It is useful to discussed possibility of creating New European Union Methodological Panel (not all, last accepted methodologies were not able to produce incomes to farmers) for assessment of different environmental practices and to be financial supported: biogas production plants (consumption of CO₂ and methane formation for production of electricity), development of new forestry's areas, new agricultural practices with lower level of application of mineral fertilizers, practicing new N₂-fixing crops, development small scale production of bio fertilizers units for N₂-fixing crops, bio fertilizers

based on *Trihoderma harzianum* for other crops and etc. Development of new systems for financial support for European Country Members working on bio and organic environmental agriculture have to be done. All EC projects abstracts of all awarded environmental projects have to be registered at ResearchGate and Academia.edu in order to be increase research interest by number of reads, recommendation's and citations. Public opinion factor to be developed which will additionally includes, opinion of scientific and non scientific readers, not peer reviewed newspapers, journals, magazines etc. Environmental value have to includes not only opinion of professionals and high level researches but opinion of ordinary people for creation of new environmental public factor. At composting of green, harvested, agricultural, town and other wastes to make new requirement to reduce danger from infection of population, to increase sanitation temperatures at composting from 55°C for 3 days to 60°C for 3 days. This will introduce, as a must, usage of microbial accelerators such as biocontrol agent *Trihoderma harzianum* (in addition *Trihoderma harzianum* have killing effect to the highest number of pathogens) which next to killing effect will prolong thermophilic stage thus sanitation period. In addition enough big volume will be needed before composting. All wastes have to be kept into improved quality depots with high sanitation requirements (town wastes can carry infections from hospitals and other private medical offices, protection from fires etc.). To all environmental projects, analyses for economic, effectiveness, ecological efficiency, protection of environment and social acceptability must be done at the end of the projects. (European Commission, Brussels, (2016), COM (2016) 157 final)

VII. Practical measures for useful implementation of EC Environmental Policy

The figures shown in Figure 1, 2 and 3 strongly support urgent measures have to be taken for protection, maintaining and improving environmental presence of the planet: Policies to support reduction by 15-20% of mineral fertilizers to all agricultural and forest plants; Policy to support reduction by 30% of N mineral fertilizers for leguminous plants; Policy to support production bio fertilizers for all leguminous plants; Policy for production manures, composts and strong extension bio and organic agriculture; Policy to support production of *Trihoderma harzianum* strains, bio fertilizer by stimulating root and top biomass and suppressing a large number of plant diseases; Policy to support changing ratio root/top plant biomass for better consumption of mineral fertilizers by roots and to maintain sustainable yields and reduce stress factors such as droughts, flooding's, early or late snowing's which reduced N₂-fixing activities etc.; Policy to support better waste management to all agricultural residues by mulching, composting, organic fertilizers production such as manures, sludge's, vine wastes, biochars (husks from sunflowers, rice, residues after extraction of oil from vine seeds, woods chips, barks, town bushes waste and all other wastes. Enzyme production and application has to be used for increasing efficiency of composting of wastes; Policy to support better management for higher food quality production and delivery at the markets as fresh as possible; Better policy to support "public factor" such as publication in newspaper, small magazines, popular publications, radio broadcastings, TV ecological movies, posters in conferences, symposiums, meetings for nature protection, advertisings etc.; Creating conditions for better regeneration of town soils already destroyed from city industrial activities and production of green biomass for better quality of air, consumption of CO₂ and composting; Large scale Reforestation of flat and mountain areas with trees, bushes and grasses with higher leave surface. Plastic management: a). experiments to be DE gradated by

enzymes produced by microorganisms, b) to be use high temperature and new formed balls and other forms thus using them as basis (lowest and top layers) for new roads, and producing new surface layer on the roads. Advantage for this activity will come because plastics are chemically neutral but very difficult to be DE gradated by microorganisms. Sea microorganisms suffered from salt content and that needed to start selection of salt tolerant microorganism which can be developed in artificial conditions and then it will be possible to attacked big accumulations of plastics in sea. Policy to support start of better water management by building small scale biogas plants using waste waters, waste town foods, green biomass in order to produce electricity and consume produced CO₂ from air. Subsidies and creating green towns and areas and substitutions of classical cars and vehicles using petrol with electrical cars and all other transportations. Building new parking places with effective air purification systems and wastewaters. Financial support for peoples to buy electrical cars, busses and vehicles. For example in San Francisco, USA 47% from total emissions in town are from cars and vehicles and 71% are from private transportation. Organizing more available information about environmental pictures in small villages, cities, big towns and industrial centers. Building more resting places at roads and towns to meet very hot day's temperatures like last days in Europe and too cold days and nights due to climate changes. (European Commission, Brussels, (2016), COM (2016) 157 final). More legal and financial measure have to be taken by EC against these countries which do not want to stop deforestation and financial support to be given to countries which support measures against worming effect of the planet.

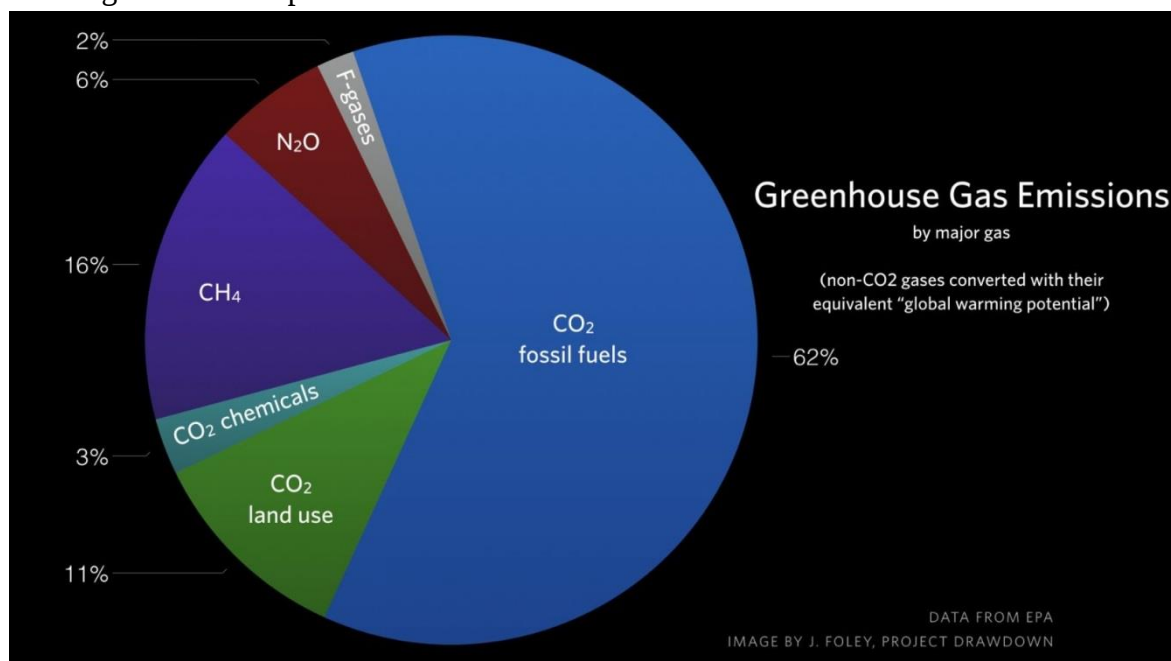


Figure.1. Distribution of Greenhouse gas emission. (Data from EPA, Image by J. Foley, Project Drawdown <https://www.drawdown.org/>)

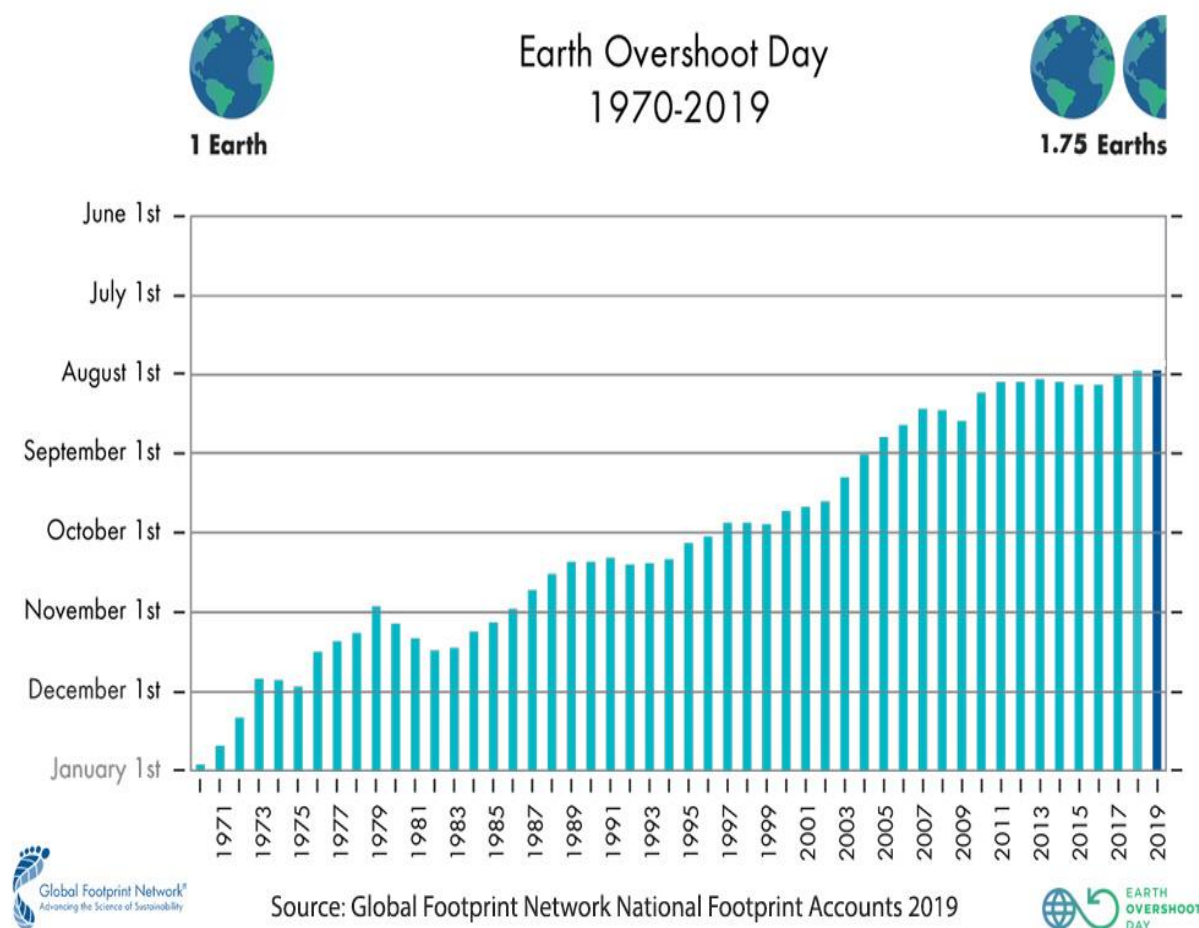


Figure 2. Footprints accounts by years; Global Footprint Network. National Footprint Accounts 2019. (<https://www.overshootday.org/>)

SHOW CASES NEEDS FASTER MEASURES AGAINST DISASTERS BY NEW LOWS AND OBLIGATIONS

It is important to note that recent disasters will stimulate EC authorities to take faster protection measures:

Russia, Siberia, Novosibirsk (8/4/2019): 3 million ha forest area are burned (or 30,000.00 km²). Totally 12 millions ha are destroyed. At the moment (17.08.2019) according to Russian authorities under fire are about 1.2 millions square kilometers. 2. Nobody can tell just now how many animals, plants, microorganisms have been burned? North behind Arctic circle: burned 784 931 ha in zone of forest ice (Arctic, Yakutia, Tundra. In addition somewhere peat has been burned: Siberian Times Reported; At the moment according to Russian authorities are under fire only 1.2 millions square kilometers in Siberia and Far East. Greenlandic warming effect (8/4/2019): melted over 11 billions ice for 24 hours. Warming temperature: -22°C.; The last (8/2/2019) hot days in Europe melted 800 million tones ice in Switzerland which will meet needs of Switzerland for 1.5 years of water, reported World Meteorological Station (also: www.varhove.com); In Bulgaria several forests places and depots have been under fires (14.08.2019) and new appeared. In addition Bulgaria at the moment is number 1 for contamination of air with SO₂. In the Brazilian states Amazonas (17.08.2019) had 1699 fires in July and in Mato Grosso 8799 fires. Totally are deforestrated

4,699.0 square kilometers in 2019 as compare with 2810 fires in 2018 which is increase of 39% as compare with 2018. The previous year are deforestrated only 2,810.0 square kilometers. This is the reason why Germany declare that they will stop financial support to Brazil for protection of environment. These fires will be real assessed in the near future but now CO₂ noted weak decrease for this year because of photosynthesis and phytoplankton in the North semi globe.

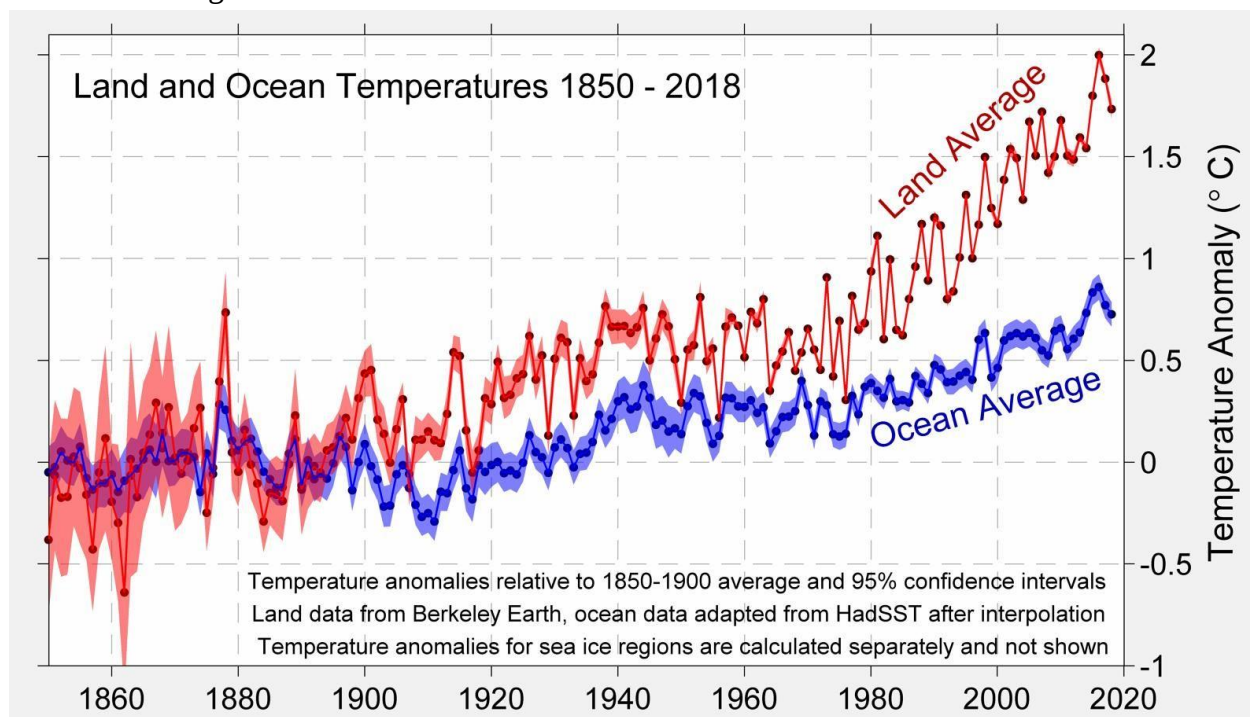


Figure 3. Land and ocean temperatures dynamics by years (<http://berkeleyearth.org/global-temperatures-2017/>)

This tendency will continue to the middle autumn. In Greenland from 31 July to 31 August this year (2019) over 58 billion tones ice have been melted This is with 40 billion tones more as compare to the middle values. This 58 billion tones do not include the amount of the ice which have be removed from icebergs and melting of ice from the wormer water. Bulgaria is at first place in the world for production of SO₂.(22.08.2019)

VIII. Reduction of climate changes already started with the following activities:

Recognizing importance of world environmental policy for development of new plants with big leave surface and density as strongest and fastest way to reduce concentration of CO₂ having in mind recent developments:

1. Switzerland Research Group make calculations and suggested:

One trillion trees can consume 830 billion CO₂ from atmosphere equal to CO₂ produced from population for 25 years; Free areas are equal to territory of USA which is 9 million m² free space suitable for accommodation of 1 billion (1,000,000,000.00) trees. Other decision will be difficult for implementation because this is the cheapest. There are examples:

A. To maintain the forest in Amazonia will support 1/5 from O₂ in the planet;

B. In Philippines there is a new law "Hose Bill 8728". According to the law graduated students from schools, colleges, universities when graduated must have planted 10 plants.

This mean 175 million plants. Their forest reduced CO₂ by 20% from towns, mining areas and in forests;

C. Ethiopia decided daily reduce CO₂ 200 million t/day and to plant 4 million per day plants for stability of climate and nature;

D. India is making 66 million plants planted per 12 hours;

E. This July of 2019 is the warmest month in our history;

F. For the last 120-140 years temperatures of waters increased by 0.5-07°C and for the surface of 2°C;

G. In Bulgaria form 15 million acidic soils 4 million (26.6%) need improving of pH. Also many new plantations were started this year; many local forest places and depots are in the fire (17.08.2019) and government took strong measures to stop fires.

Unfortunately the most suitable countries for new plantations are not EU members. They are: Russia, USA, Canada, Australia, Brazil and China. There is space for 1-1.5 million trees in the planet.

Positive balance is also needed between destroyed trees and new plantations.

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Distribution of Selected Soil Nutrients in Aggregate Sizes of Soils Under Different Geologic Formations in Southeast Nigeria.

Leonard Chimaobi Agim*, Chioma Mildred Ahukaemere,
Stanley Uche Onwudike,

Chinonso Millicent Chris-Emenyeonu, Adaku Felicia Osis,
Emmanuel Emegamha Ihem, Samuel Uche Obite

**Federal University of Technology, Department of Soil Science and Technology
P.M.B 1526 Owerri Imo State Nigeria*

Corresponding Author: Leonard Chimaobi Agim, e-mail: agimleonard@yahoo.com

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Abstract.

Soil nutrients which are major factors to crop yield and food security could be loss to erosion as a result of structural break down leading to water pollution and low crop yield. Soils of southeast Nigeria like others in the humid tropical area are prone to degradation and are low in nutrient status. Therefore the study was conducted in order to investigate the distribution of selected soil nutrients in aggregate sizes under different geologic formations namely Asu River Group (ARG), Coastal Plain Sand (CPS), Falsebedded Sand Stone (FBS) and Bende Ameki Group (BAG) in Southeast Nigeria.

At a depth of 0-15 cm, three replicate soil samples were taken from each formation. Collected samples were air dried, crushed and sieved using 2 mm mesh, properly labelled and analysed using standard methods. Samples for aggregate stability were not crushed after air drying. Core samplers were also used to collect samples for bulk density determination. Wet sieving method was used in separating samples into different sieve sizes of 2, 1, 0.5, and < 0.25 mm respectively. The experiment which was analysed using ANOVA was laid in Randomised complete block design. Significant means were separated using LSD at 5 % probability.

Result indicated significant ($P < 0.05$) variations in soil nutrients with sieve sizes. Soil organic carbon ranged from 10.30 % in aggregate diameter of 2 mm to 13.90 % in 0.5 mm in Asu River Group, 5.30% in 2 mm diameter to 12.30 % in < 0.25 mm in Coastal Plain Sand, 8.80% in 2mm sieve to 13.50 % in < 0.25 mm and in Falsebedded Sand and from 8.40 % in sieve of 0.5 mm to 15.8% in < 0.25 mm sieve size in Bende Ameki Group. Higher values of total nitrogen were noted in 0.5 and in < 0.25 mm sieve sizes. Available phosphorus was significantly ($P < 0.05$) found more in aggregates size of 1mm in all studied soils except in Uzuakoli. The stability of aggregates using percentage water stable aggregates greater 0.25 mm ($WSA > 0.25$) was significantly higher in soils of Umuna (59.18%) under False bedded Sand Stone and least at soils of Obinze (26.27%) under Coastal Plain Sand and followed the order: FBS > ARG > BAG > CPS. Result also showed that soil organic carbon had significant ($P < 0.05$) positive relation with water stable aggregates WSA ($r = 0.50$), pH water ($r = 0.53$), total nitrogen ($r = 0.79$), effective cation exchange capacity ($r = 0.51$) of the studied soils.

Key words: aggregates, geologic formation, soil nutrients, lithology, organic matter, Soil erosion.

Introduction

Soils of sub-Saharan Africa are characterized with low crop productivity (Eswaran, 1997), and witness severe degradation due to erosion, nutrient depletion, and pollution (Igwe, 2003 and Lal, 2009). In studies of soil degradation, soil aggregates and associated nutrients composition are important factors that must not be toiled with. Incompatible farm practices including continuous farming, deforestation and bush burning (Mbagwu and Obi, 2003) in addition to increase in population and the use of modern farm techniques have led to disintegration of soil aggregates thus causing soil erosion.

According to Nimmo and Perkins (2002), Singer and Munns (1996), Agim (2016), soil aggregate is an assemblage of two or more soil separates which more strongly cohere together than the surrounding mass. Stability of aggregates is the capability of the soil to stand firm following action of a disruptive force such as water, wind and ice etc (Quink and Murray, 1991). Soil aggregation is a soil quality indicator that provides information on the soil's ability to function as a basic part of the environment and influences the transportation of liquids, gases and heat as well as physical process such as infiltration and aeration (Nimmo, 1997). Aggregate sizes vary from one another and from one soil to another in their physical and chemical properties (Ihem et al., 2017). Clay content, organic matter and exchangeable cations for instance, vary from individual aggregate size fraction to another (Cambardella and Elliot, 1993; Cruvinel et al., 1999). Some researchers including Tisdall and Oades (1982), Green et al., (2005), Jiang et al., (2011) and Agim (2016) have studied nutrient content in some aggregate size. Igwe (2001) observed that smaller aggregates sizes were more enriched with soil organic carbon. On the other hand, nutrient composition, availability and uptake to crops which is the key to crop yield and food abundance has been documented to be influenced by parent materials or geology (Giesler et al., 2005 and Onweremadu, 2007). In understanding changes in soil build up and development, studies on land forms (littology and morphology) are important. Akamigbo and Asadu (1983) observed that soil geology or parent material has very significant influence on the overlying soil when the soil is formed in *situ* from the parent material. The characteristics of a parent material strongly influence the physical and chemical properties of soil aggregates. These are most strongly seen in such essential soil properties like colour, clay mineralogy, texture, structure, texture, and chemistry (Dixon, 2015). Information on nutrient distribution in aggregate sizes with respect to parent materials under study in particular is lacking (Eswaran et al., 1997).

Lack of such could be responsible for the increasing rise of low crop productivity even after applying organic and inorganic fertilizers, diversity of rills, gullies, soil structure breakdown and water pollution. Based on the above, the major objective of the study was to determine the distribution of selected soil nutrients in aggregate sizes under different geologic formations in south eastern Nigeria. Specifically the study determined the soil physical and chemical properties of the studied soils and the distribution of selected soil nutrients in different aggregate sizes and related soil properties among the studied soils.

Materials and Methods

The study was carried out at Ishiagu in Ebonyi State located on latitude 5° 27'11"N and longitude 7° 31'50.04' E, Obinze Latitude 5°22'23.3"N and longitude 7° 9'34"E, located in Imo State, Umuna in Okigwe, Latitude 5°42'N, Longitude 7°10'E, in Imo State and Uzoakoli on latitude 5°38'10.2" E and Longitude 7°33'32.1" N in Abia State representing four geologic

formations namely Asu River Group (ARG), Coastal Plain Sand (CPS), Falsebedded Sand Stone(FBS) and Bende Ameki group (BAG respectively)(FEDLAR,1990).

The Asu River Group is the first recorded marine sediments which comprises of bluish grey to brown shale and sandy shale, fine-grained micaceous sandstones and dense blue limestone (De-Swardt and Casey 1963; Reyment 1965;FEDLAR, 1990 and Ezech, 2011). It is majorly located in Ishiagu in Ebonyi State. The Coastal Plain Sands, otherwise called Beni Formation, is of the Pleistocene- Oligocene era consisting of unconsolidated yellow and white sand materials. Sometimes it was cross bedded with sandy clays, clays and pebbles (Federal Department of Agricultural Land Resources, (FEDLAR 1990). It is the largest of other formations stretching from South of Umuahia to Aba in Abia State, going beyond the mainland areas of Obehie in Rivers State, to Akwaibom State and Owerri in Imo State. They highly weathered, deep, strongly acidic and well drained (FEDLAR, 1990)

The False Bedded Sandstone (Ajali formation) are composed of thick unconsolidated, poorly sorted sandstone which are white to pale green in colour but sometimes are stained red yellow or brown by iron oxides, indicative of ferrugination (FEDLAR 1990). The Bende-Ameki Group is of the Eocene that underlies a relatively narrow strip of land North of Umuahia and the entire Bende extending westwards and joining the Nanka Sands Formation near Orlu in Imo State (Chikezie *et al.* 2010). It is made up of fine to coarse sand stones in addition to calcareous and thin shelly lime stone materials (FEDLAR,1990).This group is also highly weathered, deep and well drained and is characterised with highly dissected and convoluted terrains.

The study areas belong to the humid tropical climate which is warm all the year round (Anyadike, 2002). Mean annual rainfall ranged from 1205 mm in Ebonyi - 2700 mm in Imo State, NIMET (Nigerian Meteorological Agency), Nigeria, (2012) while yearly temperatures and humidity range from 26-29°C and 80 %- 90 % respectively (NIMET, 2012). The major vegetation of the study areas is tropical forest (Anyadike 2002), which has been tampered by anthropogenic activities. There also exists forest savanna vegetations and fresh water swamp around Afikpo, Akaeze, Abakiliki, and Okigwe and within the Riverine areas. The major economic activity in the areas is farming where oil palm plantation, palm wine tapping, cassava, maize, yam and fishing dominate others.

Soil Sampling

Soil samples were collected at random from a depth of 0 -15 cm in three replicates from each of the location making a total of twelve (12 samples used). Collected samples were air dried, crushed and sieved using 2 mm mesh, properly labelled and was taken to laboratory for analysis. Samples for aggregate stability were not crushed after air drying. Core samplers were also used to collect samples for bulk density determination. All sampling was conducted on soil under oil palm plantation in order to avoid variability apart from geologic formations.

Laboratory methods

The method of Kemper and Rosenau (1986),Mbagwu et al.,(1993) and that of Igwe (2001) were used in the determination of water-stable aggregates (WSA) an indicator of stability of aggregates. Here, 100g (W1) of air-dried soils was pre-soaked for 30 minutes in deionised water. Wetted soils were put in the topmost of a nest of four sieves of 2, 1, 0.5, and

< 0.25 mm mesh and were oscillated vertically in water for twenty (20) minutes at the rate of one oscillation per second. After wet-sieving, the remaining soil materials on each sieve were emptied into beakers, dried for 48 hours in an oven and weighed (W2). The percentage of sand in each sieve fractions was corrected by washing the aggregates with sodium hexametaphosphate, oven dried and weighed (W3). Percentage water stable aggregates (%WSA) was then calculated using $\% \text{ WSA} = \frac{W2 - W3}{W1 - W3} \times 100$Equ. 1

The same procedure apart from oven drying the soil in each sieve was used to obtain soil samples for chemical analyses in soil aggregate sizes.

Bouyoucos hydrometer method documented by Gee and Or, (2002) was used in the determination of particle size. Core method of Grossman and Reinsch, (2002) was used in bulk density determination. The method documented by Hendershot et al., (1993) was used in the measurement of soil pH in soil-water ratio of 1:2.5. Soil organic carbon in whole soil and in subsamples of aggregate sizes was measured by wet digestion method of Nelson and Sommers, (1996). Available phosphorus was measured by Olsen method (Emteryd, 1989).

The use of flame photometer according to Thomas (1982) aided exchangeable cations (potassium and sodium) determination while magnesium and calcium were determined using ethylene diamine tetra-acetic acid (EDTA) (Thomas, 1982). Effective cation exchange capacity was determined by summing the exchangeable cations as documented by Landon (1991) Brady and Weil (1999).

Data Analyses. Data were analysed with analysis of variance ANOVA. Significant means were separated using least significant difference (LSD) at 5% probability.

Results and Discussion

The results of the physical and chemical properties of the studied soils are presented in Table 1. Sand fraction ranged from 552.90 to 840.00 gkg⁻¹ and is significantly higher (p<0.05) in Uzoakoli. Clay fraction ranged from 110.00 gkg⁻¹ to 323.30 gkg⁻¹, while silt ranged from 40.00 gkg⁻¹ to 123.80 gkg⁻¹. These values were typical of soils of south eastern Nigeria (Igwe, 1995). Values of silt fraction which followed the order: ARG > FBS > CPS > BAG are low indicating high degree of weathering. Texturally, soil of Ishiagu was sandy clay loam, Obinze: sandy, Umuna and Uzoakoli were sandy loam and loamy sand respectively. The classification was in line with Esheth (1995), Akamigbo and Asadu (1983) who documented similar textures for surface horizon soils of humid tropics. Sandiness of texture could be attributed to land use, climate and geology. Soils with high sand fraction witness leaching, of high infiltration and low water retention thus incapable of supporting most crops. Differences in clay fraction are attributed to soil structure, clay movement and parent material. Bulk density ranged from 1.20 gcm⁻³ in Uzuakoli to 1.40 gcm⁻³ in Obinze. Soils whose bulk densities were low are related to high porosity, lesser compaction and easier penetration of roots and movement of micro fauna in them. Higher bulk density of soils leads to low infiltration and high runoff. However these values were lower than 1.85 gcm⁻³ (SSS 2006) considered as very critical and will surely impair root growth and is tandem with those of tropical soils (Landon, 1991).

The stability of aggregates using percentage water stable aggregates greater 0.25 mm (WSA > 0.25) was significantly higher in soil of Umuna under FBS (59.18 %) and least at

soils of Obinze (26.27 %) under Coastal Plain Sand. The trend in the stability with respect to studied parent material was FBS > ARG > BAG > CPS (Table 1). This trend is attributed to texture, type of clay (USDA 1996) and organic matter which has binding effects soil particles (Tisdall and Oades, 1982; Hayness and Swift, 1990; USDA, 1996) and their interactions (Le-Bissonnaise, 1996). Others include exchangeable sodium percentage (Kazmanet *al.*, 1983), soil management (Iraj, 2009). Kay and Angers (1999) stated that aggregate stability declines rapidly as organic carbon decreases from 1.5- 1.2%. Among the list of other factors that affect structural stability include sesquioxides (Le-Bissonnaise and Singer 1993). This result showed that soil under False bedded sand stone is much more stable than others and will be able to resist erosion more than others. Soil pH in water though did not differ significantly ($p < 0.05$) among parent materials ranged from 5.37 to 5.75 (Table 1). Moderate acidic condition of the soils was credited to constant leaching by rainfall in the area. This leaves the soil saturated with more aluminium and hydrogen (Landon, 1991).

The result of soil organic carbon presented in Table 1 significantly differed ($p < 0.05$) with parent material and followed similar trend with that of aggregate stability (FBS > ARG > BAG > CPS). Soil organic carbon (SOC) ranged from 9.60 in Obinze - 14.80 g kg^{-1} in soils under Uzuakoli. Generally, the result of soil organic matter are rated low (Landon 1991; Igwe and Stahr 2004, Opara - Nadi (1988), typical of tropical soils, a factor that predisposes the soil to dispersion making it prone to erosion (Agim et al., 2012).

Table 1. Physical properties of studied soil.

P.M	Location	Sand	Silt g kg^{-1}	Clay	T.C	B.D g cm^{-3}	WSA %	pH (H_2O)	SOC g kg^{-1}	Av. P mg kg^{-1}	T.N g kg^{-1}	ECEC cmol kg^{-1}
ARG	Ishiagu	552.90	123.80	323.30	SCL	1.25	47.16	5.37	12.40	10.94	1.20	7.41
CPS	Obinze	809.60	80.40	110.00	S	1.40	26.27	5.75	9.60	11.26	1.02	3.97
FBS	Umuna	622.90	90.40	286.70	SL	1.30	59.18	5.75	10.90	11.57	1.30	12.00
BAG	Uzoakoli	840.00	40.00	120.00	LS	1.20	31.15	5.42	14.80	11.86	1.20	3.21
LSD(P <0.05)		22.10*	7.31*	10.42*		0.21*	2.23*	NS	0.39**	NS	NS	0.95*

P.M=parent material, ARG=Asu River Group, CPS=Coastal plain sand, FBS=False bedded sand, BAG=Bende Ameki Group, WSA=water stable aggregates. BD=Bulk density. *=Significant, **=highly significant, ECEC=effective cation exchange capacity, SOC=Soil organic carbon=probability level, Av. P=Available phosphorus, T.C=Textural class.

The distribution of selected soil nutrients in aggregate sizes of studied soil

The distribution of selected soil properties in aggregate sizes of studied soils are presented in Table 2. Soil organic carbon ranged from 10.31 g kg^{-1} - 12.20 g kg^{-1} in aggregate diameters of 2 and 0.5 mm in Ishiagu (ARG), 5.30 - 9.30 g kg^{-1} in 2 and < 0.25 mm in Obinze (CPS). Similarly, values of 8.80 - 10.60 and 8.40 - 14.30 g kg^{-1} were obtained in Umuna (FBS) and Uzoakoli (BAG) under sieve sizes of 2, < 0.25 and 0.5 - < 0.25 mm respectively. Generally, these values were lower than that contained in whole soil (Figures 1:a-d). This confirms that breakdown of aggregates leads to loss of organic matter. In all cases however, organic matter were low, highest values were obtained in the 0.5 mm sieve at Ishiagu, where as they occurred at the < 0.25 mm for others. Result obtained in Ishiagu is similar to that of Igwe 2001, Green et al., (2005) where as those of others followed the trend of Razalfimbelo et

al., (2008) who reported high SOC in micro aggregates (<0.02 mm). Inconsistent values are attributed to parent materials. The high values of soil organic matter at this level of aggregation are also attributed to slaking which occur when bigger aggregates are not able to survive inner pressure as a result of fast water absorption or tillage. Such process releases heat that makes the aggregate to collapse. Igwe (2003) observed that soils whose aggregates occur more on the < 0.25 mm sizes correlate with inter rill and rill erosion in the field. Le Bissoin (1996) posited that aggregates at these sizes are very unstable and undesirable. This implies that the organic matter contained in the above soils are very much prone to erosion losses. This also supports Mbagwu et al., (1993), Obi (1982), who found significant positive association between micro aggregate stability and organic matter concentration in tropical soils.

Total nitrogen followed the same order with organic carbon. Higher values were noted in 0.5 and in < 0.25 mm sieve sizes. Wright and Inglett (2009) found similar trends in organic nitrogen distribution in aggregates of Everglades Histosols. Guan et al., (2018) also found similar result in an alpine meadow at the Damxung Grassland Tibetan Autonomous Region, northwest China. Increase in values of nitrogen at this level of aggregation is an indication of high preservability of soil nutrient micro aggregates or clay sized fractions.

Available phosphorus was significantly ($p < 0.05$) higher in aggregates size of 1mm in all studied soils except in Uzuakoli. It ranged from 2.90 – 5.70 mg kg^{-1} in sieve size of 2mm and 1mm in Ishiagu, 3.84 – 6.64 mg kg^{-1} in 0.5 and 2 mm sieves in Obinze, 6.60 – 9.60 mg kg^{-1} in sieve size of 0.25 and 2mm in Umuna and 0.10 to 9.40 mg kg^{-1} in aggregates sizes of 0.5 and 0.25mm in Uzoakoli respectively. Available phosphorus decreased as sieve sizes tends to < 0.25 mm though not in all cases (Figures 2a and b). Aguilar and Heil (1988) observed that variations in phosphorus content along a toposequence reflected differences in parent material or geology. These values were low (Landon, 1991, Enwezor 1977) and typical of soils of the eastern Nigeria. Uzoho and Oti (2005) recorded similar trend in similar soil. Igwe (2001) attributed low phosphorus availability in soils of the area to high fixation associated with the studied soils. Low phosphorus availability in tropical soil is also attributed to intense weathering and partly to the low availability of phosphorus in the aluminium and iron combination which were the dominant sources in these soils (Brady and Weil 1999). It has also been documented that low phosphorus values inhibit effective nodulation and leads to biological nitrogen fixation process of leguminous plants (Brady and Weil 1999).

Effective cation exchange capacity (ECEC) ranged from 5.77 to 9.03 cmol kg^{-1} in sieves of 2mm and 1mm in Ishiagu (ARG), from 2.20 to 2.93 cmol kg^{-1} in sieves of < 0.25 mm and 1mm, Obinze (CPS); from 5.22 to 11.13 cmol kg^{-1} in sieves of 2mm and 0.5 mm in Umuna (FBS) and from 3.04 to 3.44 cmol kg^{-1} in sieves of < 0.25 and 2 mm in Uzoakoli (BAG) respectively Table 2. Trends in effective cation exchange capacity differed significantly among parent materials suggesting that the breakdown of macro aggregates to smaller fractions during cultivation may lead to significant loss of cations. Generally higher values were obtained macro aggregates 2-0.5 mm than in micro aggregates < 0.25 . This accounts for higher stability of aggregates at macro levels a fit attributed to the binding actions of cations. Moreover, cations especially divalent ones are tightly held at the exchange complexes of macro aggregates (Jiang et al., 2011) found higher calcium and magnesium at the macro levels of stability in their work. They however obtained high levels of sodium at < 0.25 mm

confirming high level of dispersibility thus favouring erosion in the soils. ECEC like soil organic carbon in all soils are low. These values are below the critical limits for soils of South-eastern Nigeria (Enwezor et al., 1990), suggesting poor fertility status of the soil (Igwe, 2000). Ojanuga and Awojuola (1981) attributed low ECEC to the type of clay minerals prominent in the study area and differences in parent materials.

Table 2. *Distribution of selected properties in different aggregate sizes*

Parent material	Location	Sieve Sizes mm	pH (H2O)	SOC gkg-1	Av.P mgkg-1	Total nitrogen gkg-1	ECEC cmolkg-1	
Asu River Group	Ishiagu	2.00		10.31		0.99		
			5.49		2.90		5.77	
		1.00	5.67	11.39	5.70	0.98	9.03	
		0.50	5.56	12.20	5.20	1.11	7.37	
		<0.25	5.51	11.00	4.50	1.18	5.79	
			NS	0.08*	0.21*	0.02*	1.18*	
	LSD(P< 0.05)		NS	0.16*	0.05*	0.01*	NS	
	PMX Ss							
	Coastal plain sand							
	Obinze	2.00	5.63	5.30	6.64	0.98	2.55	
		1.00	5.83	7.30	4.06	1.01	2.93	
		0.50	5.58	8.30	3.84	1.02	2.43	
<0.25		5.85	9.30	4.01	1.02	2.20		
		0.23*	0.12*	1.00*	NS	0.32*		
		0.05*	0.32*	NS	NS	1.22*		
LSD (P <0.05)								
PM X Ss								
Falsebedded sand	Umuna	2.00		8.80		1.20		
			5.41		8.60		5.22	
		1.00	5.26	9.10	9.60	1.10	8.59	
		0.50	5.32	10.50	9.00	1.28	11.13	
		<0.25	5.48	10.60	6.60	1.29	9.18	
			0.27*	NS	0.03*	NS	2.14*	
	LSD (P< 0.05)		1.23*	1.23*	1.10*	NS	2.16*	
	PM X Ss							
	Uzuakoli							
			2.00		14.00		1.15	
				5.54		0.20		3.44
			1.00	5.71	9.80	3.90	1.10	3.15
		0.50	5.09	8.40	0.10	1.10	3.16	
		<0.25	5.04	14.30	9.40	0.09	3.04	
LSD (P <0.05)		1.32*	0.17*	0.31*	NS	NS		
PM X Ss		1.20*	1.76*	1.77*	NS	NS		

ARG=Asu River Group,CPS=Coastal plain sand, FBS=Falsebedded sand,BAG=Bende Ameki Group,SOC= Soil organic carbon, ECEC =Effective cation exchange capacity *=Significant,**=highly significant, P= probability level, LSD=Least significant difference. PM x Ss= Interaction between parent material and sieve sizes, Av.P=Available phosphorus

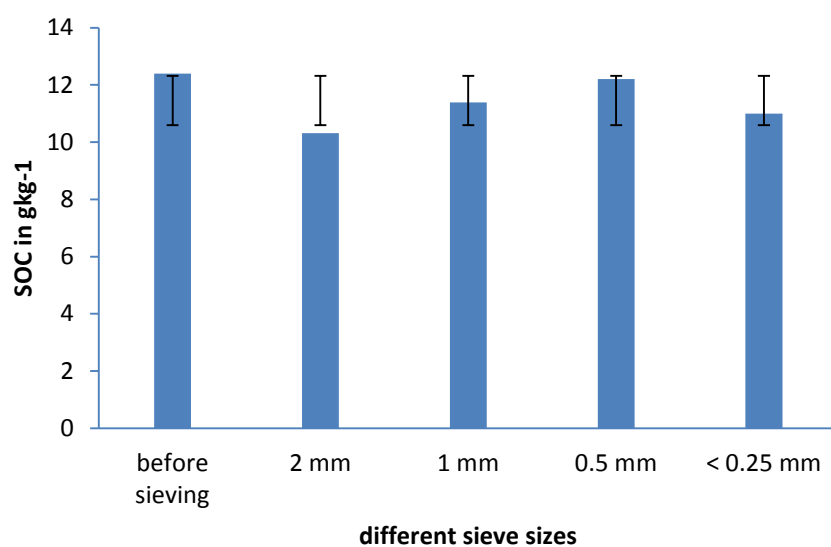


Figure 1a. Soil organic carbon in whole soil before sieving and in sieve sizes under the Asu River Group formation.

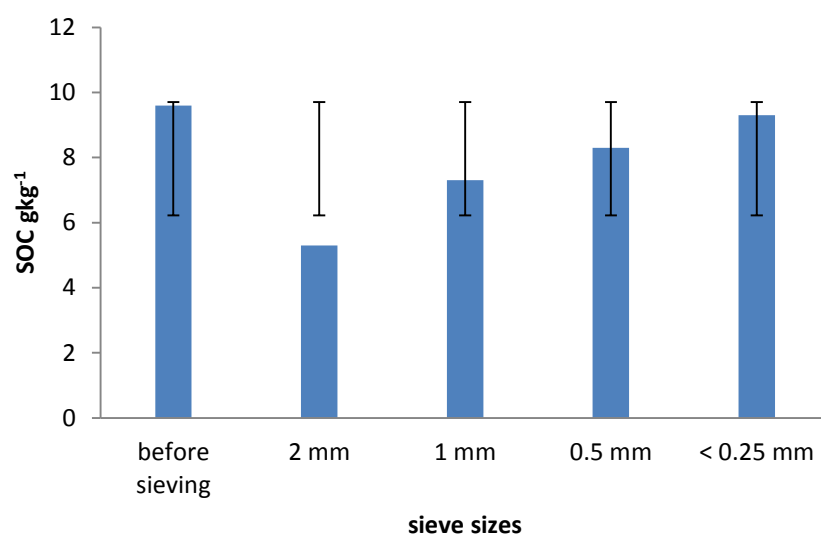


Figure 1b. Soil organic carbon in whole soil before sieving and in sieve sizes under Coastal Plain Sand.

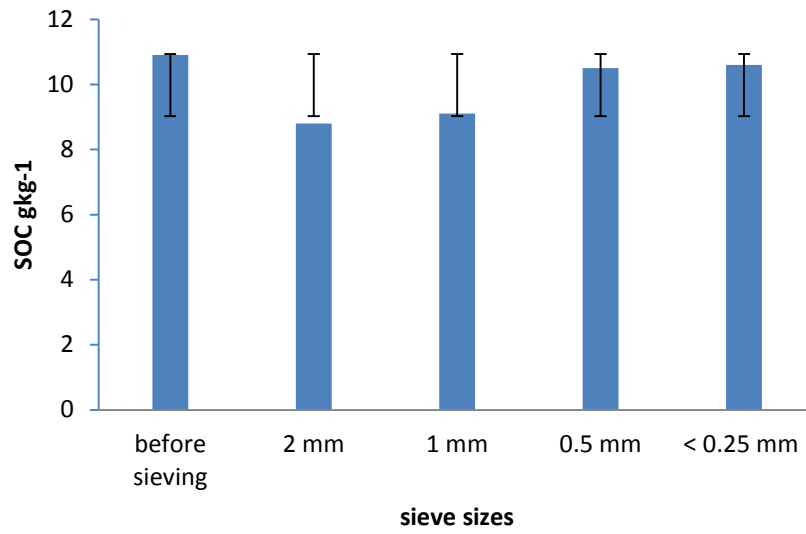


Figure 1c. Soil organic carbon in whole soil before sieving and in sieve sizes under the Falsebedded Sand Stone

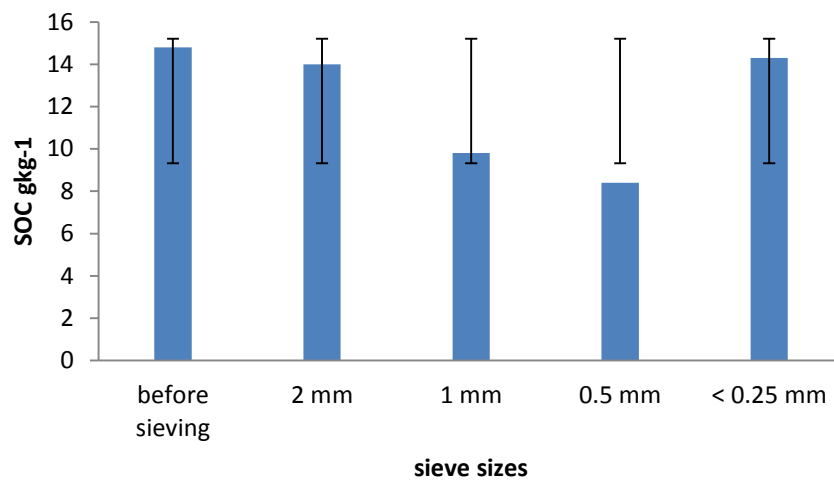


Figure 1d. Soil organic carbon in whole soil before sieving and in sieve sizes under Bende Ameki Group.

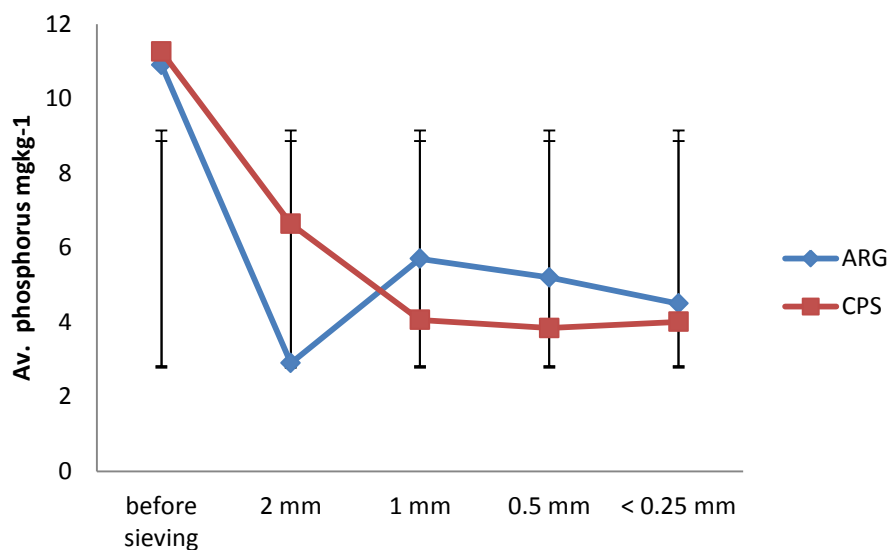


Figure 2a. Available phosphorus in whole soil before sieving and in sieve sizes under Asu River Group and Coastal Plain Sand.

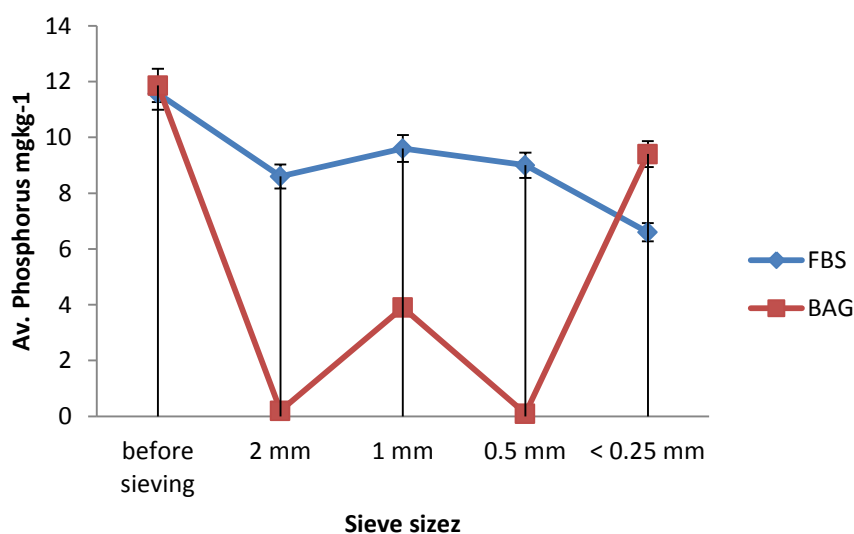


Figure 2b. Available phosphorus in whole soil before sieving and in sieve sizes under Falsbedded sand and Bende Ameki Group

Relationships among selected soil properties of studied soil.

In the result, soil organic carbon had significant ($P < 0.05$) positive relation with water stable aggregates WSA ($r = 0.50$), pH water ($r = 0.53$), total nitrogen ($r = 0.79$), effective cation exchange capacity ($r = 0.51$) and negatively related with bulk density ($r = -0.58$) Table 3. This implies that increase in organic matter content of the soil increases soil stability, soil pH, total nitrogen and effective cation exchange capacity by 50, 53 and 79 and 51 percents respectively. These results were similar to Agim et al., (2012) Sakin (2012) and confirm that of Unamba – Opara, (1982) on selected Nigerian soils. Increase in the structural stability of

the soil was as the result of binding effects of organic matter on soil properties. While organic matter gives flesh to the sand content remain the skeleton (Brady and Weil, 1999). The content of organic matter and nitrogen in soils are interwoven hence the positive relationship among them (Sakin, 2012; Unamba-Opara, 1982). This is because microbial decomposition of organic matter leads to nitrogen availability in soils. This assertion is not ignorant of the fact that nitrogen availability in soil is also achieved via synthetic fertilizer application and atmospheric fixation. Result of the relationship between organic carbon and effective cation exchange capacity supports the fact that it is a reservoir of soil cations and therefore availability of micronutrients in the soil are imminent. Onwudike *et al.*, (2016) attributed positive relations between soil organic matter, micronutrients and soil pH to chelating characteristics of organic matter which helps to hold nutrients in the soil. In his own Verma *et al.*, (2005) attributed such positive correlation to complexing agents that are generated by organic matter which promotes nutrient availability in soil. Negative relationship between soil organic matter and bulk density confirms is in order. This is because microbial decomposition of organic matter increases soil pores, thus low bulk density.

Total nitrogen related positively with moisture content and aggregate stability ($r = 0.38$, and 0.50 , $P < 0.05$). This goes further to buttress the important of organic matter in soil.

Table 3. Correlation matrix among selected properties of studied soil.

	Units	Sand	Silt	Clay	MC	BD	WSA	PH	SOC	TN	Av.p	ECEC
Sand	gkg ⁻¹	*										
Silt	gkg ⁻¹	0.29 ^{ns}	*									
Clay	gkg ⁻¹	0.98**	0.15 ^{ns}	*								
MC	gkg ⁻¹	0.48*	0.01 ^{ns}	0.57*	*							
BD	gcm ⁻³	0.46*	0.01 ^{ns}	0.52*	0.53*	*						
WSA	%	0.53*	0.05 ^{ns}	0.59*	0.89*	0.74*	*					
pH		-0.29 ^{ns}	0.11 ^{ns}	0.29 ^{ns}	0.01 ^{ns}	0.06 ^{ns}	0.16 ^{ns}	*				
SOC	%	0.22 ^{ns}	0.06 ^{ns}	0.30*	0.76*	-0.58**	0.73 ^{ns}	0.53 ^{ns}	*			
TN	%	0.15 ^{ns}	0.06 ^{ns}	0.20 ^{ns}	0.38*	0.10 ^{ns}	0.50*	0.03 ^{ns}	0.79*	*		
Av.P	mgkg ⁻¹	0.07 ^{ns}	0.07 ^{ns}	0.07 ^{ns}	0.03 ^{ns}	0.11 ^{ns}	0.34*	0.04 ^{ns}	0.02 ^{ns}	0.02 ^{ns}	*	
ECEC	cmolk g ⁻¹	0.66*	0.37 ^{ns}	0.60*	0.11 ^{ns}	0.28 ^{ns}	0.08 ^{ns}	0.31 ^{ns}	0.51*	0.09 ^{ns}	0.08 ^{ns}	1

Conclusion

In conclusion results showed that variations occur in soil nutrients among geologic formations and aggregates. Organic carbon, available phosphorus and effective cation exchange capacity of soil varied with sieve sizes. Soil organic carbon was lesser in the aggregate sizes in comparison to that of the whole soil at the beginning of the study. The stability of aggregates using percentage water stable aggregates greater 0.25 mm (WSA > 0.25) was followed the trend: FBS>ARG>BAG>CPS. Effective cation exchange capacity followed the trend ARG>FBS>CPS>BAG. Significant positive relations were noted between soil organic carbon and selected properties. Soil organic carbon is very important in the protection of aggregates from deformation, therefore efforts including cover cropping,

mulching application of organic amendment etc that improve organic matter content of the soil should be adopted. Again since soil erosion is a function of rainfall, measures such as afforestation, mulching etc that will dissipate the kinetic energy of falling rain drops before it strikes the soil surface and those that would be able to trap sediments on site are recommended.

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Fertility Status of Soils Under Silvopastoral System on Two Soil Types in Imo State, Southeastern Nigeria.



Stanley Uchenna Onwudike, Olivia Oluebube Egbufor,
Ugochukwu Nnamdi Nkwopara,
and Leonard Chimobi Agim

Department of Soil Science and Technology, Federal University of Technology Owerri, PMB 1526, Imo State, Nigeria

Corresponding Author: Stanley Uchenna Onwudike; e-mail: stanley.onwudike@futo.edu.ng

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Abstract

Understanding the fertility status of soils under different agricultural systems is imperative for sustainable crop production and ecological sustainability. This study examined the fertility levels of soils under silvopastoral system of two soil types in Southeastern Nigeria. Two towns in two states with two parent materials in the region were covered namely Owerri in Imo State with coastal plain sand and Uturu in Abia State with false bedded sand stone. Surface soil samples collected within 30 cm depth were analyzed using standard methods. Silvopastoral system and parent materials guided the sampling points. Data obtained from analyzed soil samples were statistically analyzed. Significant variations existed in the particle distribution of the soil while highest gravimetric moisture content (249.7 g/kg), total porosity (67.5%) and lowest soil bulk density (0.85 g/cm^3) were recorded in the silvopastoral lands than in non silvopastoral lands. Silvopastoral lands contained higher soil organic matter (36.88 g/kg), total nitrogen (1.87 g/kg) and exchangeable bases than non silvopastoral lands. There was higher clay content (274 g/kg) in false bedded sandstone than in coastal plain sand silvopastoral lands. The highest value of soil organic matter (36.88 g/kg) and total nitrogen (8.7 g/kg) were recorded in false bedded sandstone under silvopastoral system. There was significant negative correlation between bulk density and base saturation ($r = -0.946$) and positive relationship between total exchangeable acidity and soil bulk density ($r = 0.865$). This work revealed that parent materials under silvopastoral systems differ in soil physical, chemical and plant nutrient concentration. Therefore it is recommended that silvopastoral system should be adopted under coastal plain sand for soil fertility improvement due to its poor soil quality.

Keywords: Livestock grazing, parent materials, silvopastoral system, soil fertility,

Introduction

The world today is facing food security problem (Sasaki. et al, 2012). In order to provide enough food for the rise in human population, silvopastoral land system has been advocated (McAdam, et al., 2007). Silvopastoral system refers to a practice that involves pasture farming system in combination with varying densities of economic trees (Sasaki et

al., 2012). This method of farming is common under agro-forestry in developed countries but due the problem of limited viable agricultural lands for food production, it has spread to all parts of the world (McAdam et al., 2007).

Silvopastoral system enhances biodiversity and soil conservation (Van- Wieren and Bakker, 2008; McAdam et al., 2007) and also provides shade for cattle (Shi et al., 2010) as well as provides humidity in dry periods (Van - Wieren and Bakker, 2008). The system provides forage for ruminants (Harvey et al., 1999). Silvopastoral system has been shown to improve soil quality and enhance soil conservation and maintain environmental sustainability (Plieninger et al., 2011). Shi et al., (2010) have demonstrated that silvopastoral system improves soil organic carbon and soil macro nutrients when compared to non silvopastoral lands.

In Southeastern Nigeria, there are different parent materials such as coastal plain sand, false bedded sand stone, Imo clay shale and alluvium deposit. These parent materials have their inherent characteristics and are found in regions where silvopastoral land systems are practiced. Most of the research works on silvopastoral systems concentrated on tree species (Plieninger et al., 2011) and its effect on vegetation and yield of crops (Sasaki. et al, 2012) as well as the type of animals used in the pastoral system without putting into consideration the parent material under the silvopastoral environment. It is therefore pertinent to understand the effect of silvopastoral system on soils of different lithology for proper soil management.

Materials and Methods

This study was carried out at Uturu (latitude 5° 45'N; longitude 6° 26'N) in Abia State and Owerri (latitude 5° 22'N; longitude 6° 59'N) in Imo State both in Southeastern Nigeria. Parent materials and silvopastoral systems were used to identify the sampling locations. The two locations are within the rain forest zone. Some meteorological data like rainfall, temperature and rainfall days in the studied region are presented in Table 1. The area has average relative humidity of 79% during the raining months. Rainy season (April – October) and the dry season (November – March) are experienced in the region. The soil in Owerri has been classified as a typic haplustult (FDALR, 1985) while Uturu soil is derived from false bedded sand stone. The major parent material of soils in Owerri is coastal plain sand and this soils are known to have strong acidity, low exchangeable bases and organic matter (Onwudike, et al., 2017) while the parent material in Okigwe location is false bedded sand stone and are characterized by low organic matter and exchangeable cations with strong acidity (Onweremadu et al., 2007).

Field Study

Three soil samples were collected at 0 – 30 cm depth from four villages within the same parent material (false bedded sandstone) under silvopastoral system at Uturu in Abia State. This was repeated in non silvopastoral system. At Owerri in Imo State the same sampling procedure was carried out given a total of 48 soil samples. The samples were collected using a soil auger, packed in well labeled black nylon, air dried and sieved with 2 mm mesh sieve for laboratory analysis.

Table 1. Rainfall and Temperature Data of 2016 in the studied locations

Month	Rainfall in Uturu Abia State (mm)	Rainfall in Owerri Imo State (mm)	Total Rainfall Days in Abia	Total Rainfall Days in Imo	Temp (°C) in Abia State	Temp (°C) in Imo State
January	0.0	0	0	0	34.8	35.2
February	25.7	23.3	2	2	35.2	32.2
March	36.2	36.9	4	4	33.6	33.6
April	153.9	132.4	8	8	35.9	30.9
May	317.4	317.5	25	20	33.5	33.5
June	261.6	261.7	20	20	32.8	32.8
July	305.2	305.2	20	20	26.8	28.3
August	506.7	476.4	21	21	26.1	26.1
September	366.0	363.4	22	21	26.3	26.2
October	241.2	231.8	19	19	26.9	23.5
November	49.7	44.3	4	5	28.0	25.4
December	24.8	23.7	1	2	28.4	28.4
Total	2288.4	2216.6	146	142	Mean = 30.69	Mean = 29.675

Laboratory analysis

Soil particle sizes (sand, silt and clay fractions) were determined by hydrometer method according to Gee and Or (2002). Bulk density was determined with core sampling method using the procedure of Grossman and Reinsch (2002) as follows

$$\text{Bulk density (g/cm}^3\text{)} = \frac{\text{mass oven soil dried (g)}}{\text{volume of core sampler (cm}^3\text{)}} \dots\dots\dots \text{equation 1}$$

Total porosity (TP) was determined from bulk density using the equation

$$\text{TP} = 1 - \frac{\text{bulk density}}{\text{particle density}} \times 100\% \dots\dots\dots \text{equation 2}$$

(particle density = 2.65)

Soil moisture content was determined by gravimetric method as

$$\%MC = \frac{W_2 - W_3}{W_3 - W_1} \times \frac{100}{1} \dots\dots\dots \text{equation 3}$$

where, W_1 =weight of moisture can, W_2 =weight of air – dried soil + moisture can, W_3 =weight of oven dried soil +moisture can, %MC=percentage soil moisture

Soil pH was determined using a pH metre in soil / liquid suspension of 1: 2.5 according to Hendershot et al., (1993). Soil organic carbon was determined using chromic acid wet oxidation method as used by Nelson and Somers (1982). Total nitrogen was determined by kjeldahl digestion method using concentrated H_2SO_4 and sodium copper sulphate as catalyst according to Bremner and Yeomans (1988). Phosphorus availability was analyzed using

Olsen and Somers (1982) procedure. Mg and Ca cations were determined using Thomas (1982) method and K and Na cations were extracted using flame photometer (Thomas, 1982). Exchangeable H and Al ions were determined according to Mclean (1982) method. ECEC (effective cation exchange capacity) was mathematically computed by adding all exchangeable cations and exchangeable acidity. Base Saturation (BS) was calculated using the formula.

$$\text{BS (\%)} = \frac{\text{total exchangeable bases}}{\text{effective cation exchangeable capacity}} \times \frac{100}{1} \dots\dots\dots \text{equation 4}$$

Results obtained were subjected to analysis of variance (ANOVA). Significant treatment means were separated using least significant difference at 0.05 probability level. Relationship among soil physicochemical properties was determined using correlation analysis.

Results and Discussion

Soil physical properties of the studied locations

Results of soil physical properties of the studied locations are presented in Table 2. There were significant differences ($p = 0.05$) among soil particle size distributions, soil bulk density, soil total porosity and moisture content. Under silvopastoral lands, coastal plain sand had higher sand fraction than the false bedded sand stone. This agrees with the earlier research works of Onwudike et al., (2016) which showed that coastal plain sand has high sand fraction due to high level of weathering. However, false bedded sand stone had higher clay particles than coastal plain sand. Soil bulk density was highest at silvopastoral soils when compared to non silvopastoral land. This could be attributed to movement of animals which could compact soil particles thereby increasing the density of the soil. Anderson et al., (2010) and Papanastasis et al., (2009) reported that livestock grazing though may improve soil fertility level but the activities of the livestock may have some negative consequences on soil quality such as increase in soil bulk density. The highest moisture content was found in false bedded sand stone. This could be due to high clay fractions resulting from parent materials and this will help in moisture retention. This confirmed the previous findings of Zhao et al., (2011) that animal grazing increases soil moisture content.

Table 2. *The physical properties of the studied locations*

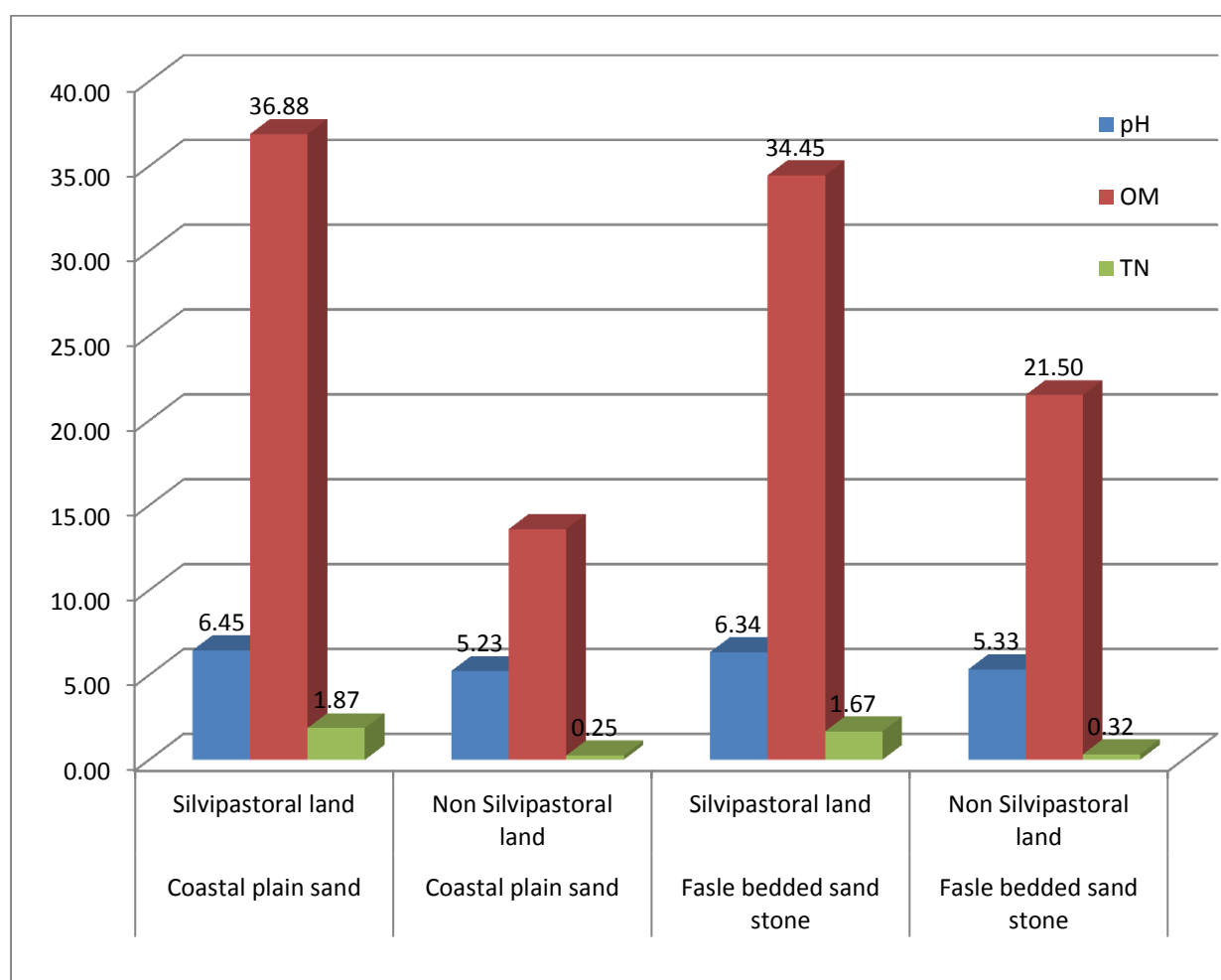
Parent material	Land use type	sand g/kg	Silt g/kg	Clay g/kg	Textural Class	BD g/cm ³	TP %	MC g/kg
CPS	Silvopastoral land	878.5	38.76	89.36	Sandy laom	1.25	52.57	122.5
CPS	Non Silvopastoral land	876.7	33.40	103.2	Sandy loam	1.24	53.08	110.1
FSS	Silvopastoral land	602.9	123.0	274.0	Loamy sand	0.85	67.54	249.7
FSS	Non Silvopastoral land	635.4	91.06	273.5	Loamy sand	1.01	61.76	172.5
	LSD _(0.05)	12.4	23.4	14.3		0.05	3.65	11.8

CPS = coastal plain sand; FSS = false bedded sand stone; LSD = least significant difference

Distribution of organic matter, soil pH and total nitrogen in the studied location

Effect of silvopastoral system on soil organic matter, total nitrogen and soil pH are presented in Figure 1. Results showed that coastal plain sand in non silvopastoral system

recorded the lowest soil pH followed by false bedded sand stone. Higher organic matter was recorded in silvopastoral lands than non silvopastoral lands. This observation was similar to the previous results as recorded in the works of Shi et al., (2010), Smit and Kooijmani (2001) and Beukes and Cowling (2003) who observed that livestock grazing increases soil organic matter. Silvopastoral lands recorded higher soil pH than non silvopastoral lands. The highest soil pH of 6.45 was recorded in coastal plain sand under silvopastoral land. Higher soil pH as found in grazed lands as compared to non-grazed lands could be attributed to animal droppings which contain higher organic matter that can reduce the acidity of the soil. Silvopastoral lands had higher soil organic matter content when compared on non silvopastoral location. The highest total N (1.87 g/kg) was recorded in coastal plain sand under silvopastoral system. Higher organic matter and total N in grazed lands could be attributed to animal litters with increased soil pH.



OM = organic matter (g/kg), TN = total nitrogen (g/kg)

Fig. 1. Distribution of organic matter, soil pH and total nitrogen in the studied location

There were significant differences ($p = 0.05$) among other soil chemical properties such as available phosphorus, exchangeable bases, base saturation and effective cation exchange capacity in silvopastoral and non silvopastoral systems (Table 3). The highest available P (2.57) was recorded in silvopastoral false bedded sand stone while the lowest (1.39) was in non silvopastoral coastal plain sand. This could be due to animal waste

deposits. The same trend followed in exchangeable bases and ECEC. There is therefore need to utilize the available nutrients in silvopastoral system for crop production

Table 3. Some chemical properties of the area.

Parent material	Land use type	Avail. P	Ca	Mg	K	Na	TEB	TEA	ECEC	BS
		Mg/kg	←			Cmol/kg	→			%
CPS	Silvopastoral land	2.07	2.25	1.57	0.22	0.10	4.14	1.62	5.74	72.49
CPS	Non Silvopastoral land	1.39	1.93	1.07	0.15	0.08	3.23	1.23	4.43	73.33
FSS	Silvopastoral land	2.28	2.07	1.30	0.20	0.15	4.01	0.72	4.73	84.56
FSS	Non Silvopastoral land	1.68	1.93	1.27	0.13	0.09	3.42	0.63	4.06	84.38
	LSD(0.05)	0.35	0.13	0.55	0.11	0.02	0.69	0.01	0.21	2.66

CPS = coastal plain sand; FSS = false bedded sand stone; LSD = least significant difference

Relationship among soil properties

Table 4 showed the relationship among soil properties in the studied locations. Results showed that base saturation significantly correlated negatively with bulk density ($r = -0.946$) and sand ($r = -0.996$) but correlated positively with total exchangeable acidity ($r = 0.865$), moisture content ($r = 0.864$), total porosity ($r = 0.948$) and silt ($r = 0.951$). Also soil moisture content, total porosity and soil particle sizes has significant relationship with some soil chemical properties as shown in Table 4. Reduction in bulk density due to animal wastes in silvopastoral lands increased base saturation, soil organic matter and total N which increased exchangeable bases and ECEC since according to Onwudike et al., (2016), soil organic matter acts as a reservoir for macro and micro nutrients which favor positively soil reactions and microbial activities in the soil. Increase in organic matter due to animal litters could help to reduce soil bulk density and increase total exchangeable bases. This will result to a decrease in soil bulk density since negative correlation existed bulk density and total exchangeable bases. This is because increase in organic matter will help to increase soil microbial population whose through their translocations, improves soil aggregation and aeration that reduces soil bulk density.

Table 4. Relationship among soil properties.

Property	BD	Clay	MC	TP	Sand	Silt
BS	-0.946**	0.476	0.864**	0.948**	-0.996**	0.951**
Avail. P	0.516*	-0.390	-0.633*	-0.514*	0.464	-0.572*
ECEC	0.415	-0.592*	-0.229	-0.419	0.521*	-0.373
K	0.051	-0.310	0.155	-0.057	0.217	-0.021
Mg	0.101	-0.153	0.024	-0.102	0.098	-0.025
OM	-0.272	0.097	0.433	0.268	-0.181	0.327
Ph	-0.187	-0.046	0.375	0.182	-0.048	0.228
TEA	0.865**	-0.953**	-0.741**	-0.868**	0.927**	-0.849**
TEB	-0.195	-0.006	0.371	0.191	-0.083	0.245
TN	-0.151	-0.084	0.342	0.146	-0.009	0.191

*and ** = significant difference at 0.01 and 0.05 probability level respectively

Conclusion and Recommendation

Silvopastoral systems under coastal plain sand and false bedded sand stone differ in physical and chemical characteristics with non silvopastoral systems. This research showed that silvopastoral systems under false bedded stand stone contained higher values of organic matter, total nitrogen and basic cations which are vital for crop production than silvopastoral systems under coastal plain sand. Therefore due to poor fertility level of soil under coastal plain sand in non silvopastoral system, it is recommended that this system of farming should be practiced on coastal plain sand to boost its fertility for crop production.

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Effect of Oil Spillage on Selected Heavy Metals Concentration in the Soils of Ihugbogo in Ahoada East, Niger-Delta, Nigeria.

S.N. Obasi*, C.M. Ahukaemere**, G.D. Aloni***, C.C. Obasi****

**Department of Crop and Soil Science, National Open University of Nigeria, Faculty of Agriculture, Kaduna Campus*

***Department of Soil Science and Technology, Federal University of Technology Owerri, Nigeria*

****Department of Agricultural Technology, Imo State Polytechnic Umuagwo, Nigeria*

*****Department of Crop Science and Horticulture, Nnamdi Azikiwe University Awka, Nigeria*

Corresponding Author: S.N. Obasi, +234803449915; e-mail: nobasi@noun.edu.ng

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Abstract

This study was carried out in Ihugbogo community, Ahoada East, Southern Nigeria- a community where Total E & P Nig. Ltd has carried out oil exploration and drilling dating back to over thirty years. This has led to a number of spillages on most arable soils in a community where peasant farming is a major occupation. Three locations were selected for the study, and designated as Location A, B and C which had experienced spillage in 1995, 2002 and 2007 respectively. Causes of spillage ranged from activity of vandals, leakage or explosion of the piping materials and or pressure from the crude oil products. This research however, sought to investigate the effects of the crude oil spillage on the selected heavy metals concentration of the soils as excess dosage of heavy metals on soils and invariably crops may lead to adverse health effect on man and animals which depend on crops for survival. The selected heavy metals studied were Chromium (Cr), Cadmium (Pb) and Lead (Pb). Results obtained indicated that Chromium and Lead were within the allowable limits (< 100 mg/kg) while Cd had value beyond the allowable limits (>3.0 mg/kg) according to World Health Organization. Physical and Chemical Properties of the studied soils indicated that the soils ranged from Sandy loam in locations A and B to Sandy in Location B. Available P was very low (<5.0 mg/kg) in locations A and B and moderate (5 – 15mg/kg) in location C while the exchangeable bases were very low as Ca was <2.0 cmol/kg, K and Na were <0.1 cmol/kg in locations A, B and C except Mg which was moderate (1.5 – 3 cmol/kg) in locations A and B and low (< 1.5 cmol/kg) in location C when the threshold limits were considered. There was a very strong and positive correlation between the heavy metals studied and soil organic carbon. For the studied soil to be very fit for agricultural productivity, liming will be necessary to reduce the soil acidity while organic and inorganic materials will be needed to enhance the nutrient element status of the soil.

Key words: oil spillage, heavy metals, soil nutrients, soil properties, ihugbogo community

Introduction

Anthropogenic activities have presented a growing environmental problem affecting food quality and human health in the Niger Delta Region of Nigeria. Nigeria as a major producer and exporter of crude petroleum oil continues to experience oil spills and this exposes the environment to hazards and its attendant effects on agricultural lands as well as plant growth and development (Agbogidi et al., 2005). Soil is the valuable natural resources of a nation whose quality determines its capability to function well for many intended uses (Onweremadu et al., 2007). Food is the most basic of human need for survival, health and productivity (Smith, 2006) but land degradation brought about by prolonged interface between human induced and natural factors exacerbated low food productivity (Di Falco et al., 2006) as well as its quality. One of the problems of land degradation is the accumulation of toxic heavy metals such as Mercury, Chromium, Lead, Copper, and Cadmium etc in agricultural soil (Isirimah et al., 2003).

Heavy metals concentrations in southern Nigeria soils include input from oil spillage (Roulet et al., 1999). Those from the commercial fertilizers, living materials sewage sludge, atmospheric deposition (Sensesi et al., 1999) and repeated application of organic manures, fungicides and pesticides (Li et al., 1997). Nevertheless, some of these heavy metals are naturally occurring and possibly from weathering of rocks but their concentration in the pedosphere increases due to anthropogenic inputs (Li et al., 1997). These heavy metals when present in the soil tend to decline the quality of the soil for many intended uses. As such incorporation of these heavy metals in the soil is one of the constraints to the use of waste as soil treatment (Warman et al., 1999). Pasture and crop plants act as vehicles for transferring these heavy metals and other toxic constituents into the soil and hence into the food chain (Onweremadu et al., 2006). However, the mobility of metals from solid to solution in the soil is mainly controlled by sorption – adsorption, chelating, precipitation, and oxidation – reduction process of the metal in soil (Basta et al., 2004). Some plants accumulate these heavy metals in their tissues where these constitute serious health hazards to man, grazing animals and the environment (Ellis et al., 2003).

The chronic problems associated with long term heavy metals exposure, include serious hematological and brain damage, anemia and kidney malfunctioning (Sonayi et al., 2009). Heavy metals such as Pb and Cd are lethal even in very small dose. Lead has a negative influence on the somatic development, decreases the visual acuity and acidities thresholds (Simeonov et al., 2010). Acute exposure to lead causes brain damage, neurotically symptoms, brain damage and could lead to death (Simeonov et al., 2010). Cd exposure on the other hand, causes renal dysfunction, calcium metabolism disorders and also increased incidence of some forms of cancer possibly due to the inhibition by Cd of DNA mismatch remediation (Kumar, 2009). Malignant Neoplasia and skin ulcers have been reported due to various occupations with exposure to chromium compounds. Chromium VI inhalation is responsible for bronchial asthma (Sarkar, 2005). In Ihugbogo Community, farming is the major occupation of the people within a farm land where Total E&P Nig. Ltd pipe line pass across. Therefore, the accumulation of heavy metals in soils of Ihugbogo Community is gotten from crude oil spillage. The objective of this research was to investigate the effect of oil spillage on heavy metals concentration of Ihugbogo soils in Ahoada East, Southern Nigeria.

Materials and Methods

Study Area - Location

Ahoda is located on the Latitude 5° 07'01" and 5° 4'26"N and Longitude 6° 39'12" and 6° 65'01"E. Elevation is below 100m above the sea level. The rainfall distribution is seasonal, rain occurs, on the average, every month of the year, but with varying duration. It is characterized by high rainfall, which decreases from south to north. Total annual rainfall ranges from 2,700mm to 3,500mm in the region. The maximum monthly temperature ranges from 28°C to 33°C, while the mean minimum monthly temperatures are in the range of 17°C to 24°C. The hottest months are February to April. The difference between the dry season and the wet season temperature is only about 2°C. Relative humidity is high (91 – 94%) throughout the year and decreases slightly in the dry season.

Table 1. Location Coordinates of Study area

Location	Long.	Lat.	Elevation (m)
ILA	6° 65"	5° 19"	60
ILB	6° 54"	5° 23"	60
ILC	6° 60"	5° 11"	61

ILA, B and C: Ihugbogo locations A, B and C

Socio-economic Activities

About 50 percent of the active labour force engages in one form of agricultural activity or another in which about 30 percent are women. The predominant food crops in the area are yam, cassava, plantain, maize, cocoyam, and vegetable. The dominant trees are mahogany (*Angio spp*), Obeche (*Protobullas spp*) and Iroko (*Cassia spp*).

Field Work

A reconnaissance study was carried out and the study location identified in Ihugbogo community along an oil pipeline track that cuts across major farmlands in the area. The three major locations investigated, designated as Location A, B and C had experienced spillage in 1995, 2002 and 2007 respectively. The spillage had been caused by TOTAL E&P Nig. Ltd pipeline. About five samples were collected in each of the locations and subjected to laboratory analysis to determine the effect of oil spillage on the selected heavy metals such as; Lead (Pb), Chromium (Cr) and Cadmium (Cd) concentration of the soils as well as soil physical and chemical properties.

Laboratory Analysis

The following soil properties were determined by standard routine laboratory methods as follows: The particle size distribution was determined by hydrometer method according to the procedures of (Gee and Or, 2002), Bulk density was measured by core method (Grossman and Reinsch, 2002). Porosity was computed from bulk density and particle density. Soil pH was determined potentiometrically in 1:25 soil liquid ratio (Hendershot et al., 1993). Organic carbon was determined using method described by (Nelson and Sommers, 1982) and

the result of organic carbon was multiplied by 1.724 to determine the organic matter content. Total available phosphorus was determined using Bray II method (Olsen and Sommers, 1982). Total Nitrogen was determined using Kjedal Digestion and Technicon/Auto analyzer method. Exchangeable base was determined by extraction of ammonia acetate (NH_4OAc) at pH 7.0 known as extractant in determining calcium, magnesium while sodium and potassium was determined using flame photometer. The exchangeable acidity was determined using extraction of exchangeable H^+ and Al^{3+} with KCl and titrated as outlined by (McLaren et al., 1994). The effective cation capacity was estimated by the summation of all the exchangeable base and acidity.

Statistical Analysis

Coefficient of variation (C.V) ranked as follows: low variation $\leq 15\%$, moderate variation $> 15 \leq 36\%$. High variation $> 35\%$ was used to estimate the degree of variability of soil properties (Wilding et al., 1994).

Results and Discussion

Soils physical properties of the investigated soils were as shown in table 2 where soil texture were dominated by sand and loamy sand in all investigated soils as highest sand occurred at location C (85.36%), followed by location A (76.36%) while Location B indicated lowest content (59.76%). The means of silt and clay contents were 17.08, 30.88, 10.80 and 6.56, 7.36, 6.56% for silt and clay contents in locations A, B and C respectively. Bulk densities were high in locations C (1.66 g/cm^3) and A (1.64 g/cm^3) while location B (1.57 g/cm^3) indicated the lowest bulk density. The high bulk densities distributions in the investigated soils may have resulted due to high preponderance of sand especially as seen in locations C and A respectively. Bulk density values were less than the acceptable limits of 1.85 g/cm^3 as suggested by Akamigbo 1999.

Table 2. Mean of Selected Soil Physical Properties in the three Locations

	SAND (%)	SILT (%)	CLAY (%)	Bulk Density (g/cm^3)	TC
Location A	76.36	17.08	6.56	1.64	LS
CV (%)	9.7	36.4	27.2	2.3	
Location B	59.76	30.88	7.36	1.57	LS
CV (%)	9.6	15.5	53.2	2.7	
Location C	85.36	10.8	6.56	1.66	S
CV (%)	3.1	62.1	46.2	2.3	
Lsd (0.05%)	NS	NS	NS	NS	

Coefficient of variation of physical properties indicated that sand varied lowly in all the investigated locations; $\text{CV} < 15\%$ scoring 9.7, 9.6 and 3.1 % in Locations A, B and C respectively. Silt had moderate variability in location B (15.5%) and high variability in Locations A and B where they scored 36.4 and 62.1% respectively. Clay however varied moderately ($\text{CV} > 15 \leq 35\%$) in location A and highly ($\text{CV} > 35\%$) in locations B and C. Bulk density varied lowly ($\text{CV} < 15\%$) in all investigated locations.

Table 3. Means of Soil Chemical Properties in the three Locations

SAMPLE	pH	pH	OC	TN	Av. P	Ca	Mg	K	Na	Al ³⁺	H ⁺	TEA	TEB	ECEC	%BS
Location A	(H ₂ O)	(KCl)	(%)	(%)	(mg/kg)	←				Cmol/kg					→
MEAN	5.484	4.866	1.68	0.286	3.942	0.784	1.744	0.004	0.005	0.48	0.334	0.84	2.639	3.5004	67.542
CV (%)	6.8	2.9	9.7	95.3	21.9	94.1	91.4	18.2	24.6	21.6	54.9	16.0	73.0	64.9	34.1
Location B															
MEAN	5.334	4.836	1.7434	0.163	3.763	0.856	1.078	0.003	0.005	0.536	0.332	0.87	1.939	2.813	62.873
CV (%)	2.8	4.0	7.4	15.1	36.9	91.4	76.6	37.8	82.6	13.8	26.5	13.9	65.2	43.9	29.6
Location C															
MEAN	5.528	4.65	0.85	0.204	5.138	1.072	0.614	0.002	0.009	0.482	0.376	0.818	0.896	2.18	54.551
CV (%)	5.2	5.1	25.5	157.3	26.3	51.5	72.9	18.7	3.1	19.4	26.2	14.0	58.2	33.6	35.5
Lsd	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS
(0.05%)															

OC= Organic Carbon, Av.P= Available Phosphorus, TEA= Total exchangeable acidity, TEB= Total exchangeable bases, ECEC= effective cation exchange capacity, %BS=percentage base saturation

Soils pH was both measured in water and in KCl as pH in KCl would release internally held reserved acidity of soils (Table 3). It is however noticed that pH in KCl was lower than the pH measured in water. The pH in the various locations as measured in KCl were 4.866, 4.836 and 4.65 in locations A, B and C respectively. This pH is highly acidic as it falls below the acceptable pH range of 5.5 -6.5 in arable soils (Tabi et al 2012). The high acidic content may not have resulted entirely due to oil spill as most soils in the southern Nigeria have been known to be highly acidic, fragile and leached (Iheka et al., 2015).

Organic carbon content was moderate in locations A (1.68%) and B (1.743%) while it is low in location C (0.85%). Total Nitrogen also follows the same trend; 0.286, 0.163 and 0.204% in locations A, B and C respectively. It is worthy to note that organic carbon and total nitrogen are a function of organic matter content of soils (Obasi et al., 2015). Although the results obtained on organic carbon were moderate and low, in the investigated soils, oil spill tend to increase the organic carbon content of soils (Marinescu et al., 2010). However, the duration of this spillage having taken a long while (1995, 2002 and 2007 in locations A, B and C respectively) may have contributed to the recuperation of the studied soils. This recuperation is enhanced through the activities of microbial organisms in the decomposition of litter and mineralization or organic compounds leading to phyto-remediation.

Available P contents of these soils were very low on the scale of critical limits of available P in the tropical soils. Mean available P content of the studied locations were 3.942, 3.763 and 5.138 mg/kg in locations A, B and C respectively. The expected moderate available P ranges from 5 – 15 mg/kg. Therefore, location C tends to have a relatively acceptable available P content.

Calcium, Potassium and Sodium were very low in the investigated soil. Ca had 0.784, 0.856 and 1.072 cmol/kg, K had 0.004, 0.003 and 0.002 cmol/kg Na had; 0.005, 0.005 and 0.009 cmol/kg while Mg had 1.744, 1.078 and 0.614 cmol/kg all in locations A, B and C respectively. Only Mg in location A had the moderate Mg requirement of >1.5 cmol/kg according to Tabi et al 2012 who gave the moderate Mg requirement as 1.5 – 3.0 cmol/kg. Total exchangeable bases (TEB) scored 2.639, 1.939 and 0.896 cmol/kg in locations A, B and C respectively. Effective cation exchange capacity (ECEC) also recorded 3.5004, 2.813 and

2.18 cmol/kg in locations A, B and C. The base saturations were 67.542, 62.873 and 54.551% in locations A, B and C.

The implication of the low contents of exchangeable bases follows the fact that the studied soils will likely struggle to provide the nutrient elements needed for plants growth and development. Exchangeable bases are nutrient elements adsorbed in the clay complex of soils and made available to the roots nodules of crops. The effects of oil spillage on these soils may have included fixation of these nutrients as well as reduction of soil aeration leading to the choking of soil fauna. This situation will ultimately reduce the mineralization activities taking place in the soil thereby immobilizing the few available nutrient elements.

The pH in water and KCl all had low variability ($CV < 15\%$) in all investigated locations. Organic carbon and Total Nitrogen had low variability ($CV < 15\%$) in locations A and B and moderate ($CV > 15 \leq 35\%$) in location C. Total exchangeable bases varied highly ($CV > 35\%$) in all locations while ECEC varied highly in locations A and B and moderately ($CV > 15 \leq 35\%$) in location C while Base saturation varied moderately ($CV > 15 \leq 35\%$) in locations A and B and highly ($CV > 35\%$) in location C. There was however no significant difference in all investigated soil properties at the three locations of the studied area.

Table 4. Heavy Metals in Crude Oil Spilled Site in Ihugbogo under TEPN Pipeline

Parameter	Location A (mg/kg)					Mean
	ILA 1	ILA 2	ILA 3	ILA 4	ILA 5	
Cr	3.776	3.168	3.789	3.512	3.513	3.551
Pb	6.2	6.48	6.512	6.10	6.211	6.286
Cd	3.04	2.944	2.961	2.10	2.20	2.649
Location B						
	ILB 1	ILB 2	ILB 3	ILB 4	ILB 5	
Cr	3.888	3.16	3.221	3.711	3.598	3.515
Pb	6.688	6.768	6.910	6.661	2.752	5.954
Cd	3.20	3.168	3.442	3.510	3.11	3.286
Location C						
	ILC 1	ILC 2	ILC 3	ILC 4	ILC 5	
Cr	2.294	2.08	2.981	2.611	2.501	2.493
Pb	2.752	2.312	2.910	2.512	2.322	2.561
Cd	1.344	1.504	1.982	1.332	1.291	1.490

ILA = Ihugbogo location A, ILB = Ihugbogo location B, ILC = Ihugbogo location C

The three heavy metals considered in the studied sites were Chromium (Cr), Lead (Pb) and Cadmium (Cd) as shown in Table 4. Chromium had means of 3.551, 3.515 and 2.493 mg/kg in locations A, B and C respectively. Lead had means of 6.286, 5.954 and 2.561 mg/kg in locations A, B and C respectively. Cadmium however recorded 2.649, 3.286 and 1.490 mg/kg in locations A, B and C respectively. When the minimum allowable limits were considered according to World Health Organization (WHO), Cr and Pb were within the acceptable limits in the studied soils while Cd was higher than the allowable limits of 3.0 mg/kg (Atieno et al., 2011). Also when the minimum allowable limits of countries like Poland, United Kingdom, United States of America and Australia were considered (Mantaz and Chowdhary 2006); Cr and Pb were within the allowable range while Cd falls beyond the

allowable limits of Poland, United Kingdom and United States of America, whereas it falls within the allowable limits of the country of Australia.

Table 5. *Correlation of some soils properties with Heavy metals*

	%BS	Av. P	Al ³ Sat	Ca	Cd	Cr	ECEC	OC	Pb	TEB	pHKCl
%BS	1										
Av. P	-0.407	1									
Al ³ Sat	-0.325	0.0662	1								
Ca	0.6204	-0.2646	-0.6112	1							
Cd	0.3773	-0.5501	0.1326	0.0979	1						
Cr	0.4580	-0.5701	-0.1724	0.3654	0.8019	1					
ECEC	0.9194	-0.2568	-0.4050	0.7426	0.2469	0.3731	1				
Mg	0.7796	-0.0341	-0.1620	0.3591	0.1618	0.2321	0.8341				
OC	0.5480	-0.3005	0.0399	0.3170	0.6671	0.7008	0.5313	1			
Pb	0.3038	-0.3359	0.1755	-0.0254	0.7835	0.7483	0.1744	0.7364	1		
TEB	0.9085	-0.2368	-0.4643	0.7445	0.2415	0.3638	0.9953	0.5146	0.1689	1	
pH_KCl	0.2507	-0.1118	-0.6594	0.3315	-0.2200	-0.052	0.3312	0.2484	-0.393	0.369	1

Table 6. *Mean and Range of Current Study in Comparison with WHO (2006) Maximum Allowed Limits*

Parameters	Mean $\pm$ SE (Range of present study in mg/kg)	WHO values (mg/kg)
Cr	3.551 – 2.493	100.00
Pb	5.954 – 2.561	100.00
Cd	3.286 – 1.490	3.00

WHO Values Source: Mantaz and Chowdhary (2006); Atieno *et al.*, (2011)

Table 7. *Shows the MAL for different Countries in Comparison to the levels Obtained in the Study*

Element	Poland	UK	USA	Australia	Mean obtained in Current study mg/kg
Cr	100.000	50.000	100.000	100.000	3.515
Pb	100.000	100.000	200.000	100.000	5.954
Cd	3.000	3.000	0.7.000	5.000	3.286

Source: Mantaz and Chowdhary (2006)

The correlation of studied heavy metals with some selected soil properties were as shown in Table 5. Cadmium correlated highly and negatively with available P, it correlated highly and positively with Cr, Organic Carbon and Pb. Chromium correlated highly and negatively with available P, highly and positively with Cd, Organic C and Pb. Lead correlated highly and positively with Cd, Cr and Organic C. the studied heavy metals however had low correlation with all other studied soil properties. This study agrees with that of Onweremadu and Duruigbo (2007) and Nkwopara et al (2012) that heavy metal such as Cadmium have strong and positive correlation with soil organic carbon.

Conclusion

The investigated soils were very acidic, very low in exchangeable cations as well as low available P. The effects of oil spillage on these soils may have included fixation of these

nutrients as well as reduction of soil aeration leading to the choking of soil fauna. This situation will ultimately reduce the mineralization activities taking place in the soil thereby immobilizing the few available nutrient elements. The studied heavy metals all had strong and positive correlation with organic carbon. Cadmium correlated highly and negatively with available P, it correlated highly and positively with Cr, Organic Carbon and Pb. Chromium correlated highly and negatively with available P, highly and positively with Cd, Organic C and Pb. Lead correlated highly and positively with Cd, Cr and Organic C. the studied heavy metals however had low correlation with all other studied soil properties. These soils need inputs that would neutralize the high acidity such as liming as well as use of fertilizer and organic materials to enhance the nutrients need of the studied soils.

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Physicochemical Profiles of Various Bioremediated Petroleum Contaminated Sites in Ogoniland, Nigeria.

V. T. Jason-Ogugbue*, P. C. Mmom**, I. Etela***, J.A. Orluchukwu****

* *Centre for Oilfield Chemicals Research, University of Port Harcourt.*

** *Department of Geography and Environmental Management, University of Port Harcourt*

*** *Department of Animal Science, University of Port Harcourt*

**** *Department of Crop and Soil Science, University of Port Harcourt*

Corresponding Author: V. T. Jason-Ogugbue, e-mail: tovo_jason@yahoo.com

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Abstract

This study was carried out to evaluate the physicochemical statuses of bioremediated sites in Ogoniland (K-Dere, Bodo, and Biara), Rivers State, Nigeria after a certified bioremediation protocol. Three bioremediated soils of different fallow ages (6 months, 12 months, and 18 months after bioremediation-AB) and an uncontaminated soil (Bera) were collected and analyzed for various parameters- pH, electrical conductivity (EC), total organic matter (TOM), particle size distribution, cation exchange capacity (CEC), nitrogen and phosphorus, heavy metals (lead, cadmium, nickel and copper), total petroleum hydrocarbons (TPH), poly aromatic hydrocarbons (PAH), and intermediary metabolites. Results obtained indicate that the particle size distribution of the four soil samples were similar in terms of their content of sand, silt and clay. The pH of 12m-AB and 18m-AB bioremediated soil samples were 6.34 and 6.50 respectively and were slightly lower than pH of uncontaminated soil. The EC as well as the CEC of the bioremediated soil samples were considerably lower when compared to the uncontaminated soil sample. The range of values for TOM was between 0.095 – 1.232 % with 6m-AB soil having the least value; whereas 0m-AB and 12m-AB had the highest value of 1.232 %. Sample 18m-AB had the highest concentration of nitrogen whereas, 12m-AB sample had the least concentration. The phosphorus content in each bioremediated soil was significantly lower than in uncontaminated soil. The residual TPH content of each bioremediated soil sample was above the recommended EGASPIN target TPH value of 50 mg/kg but below the intervention level of 5,000 mg/kg. The TPH contents in bioremediated soil samples were 161.25 mg/kg (6m-AB), 51.72 mg/kg (12m-AB) and 91.50 mg/kg (18m-AB). TPH was not detected in the uncontaminated soil sample. All four samples had no trace of PAH. Heavy metals were below detectable limits in all soil samples. Screening of the soil samples using gas chromatography-mass spectrometer revealed a number of metabolic intermediates in bioremediated soil samples when compared to the uncontaminated pristine soil (control). Some of the identified metabolites are known carcinogens and are deleterious to plant growth thus suggesting the unhealthy status of the bioremediated soils for agricultural productivity.

Key words: bioremediated sites, TPH, metabolites, heavy metals, soil

Introduction

Presently, the contamination of the natural environment by petroleum hydrocarbons is of enormous concern and the ever-increasing demand for petroleum products by emerging economies has worsened the problem. In order to meet this demand, there has been increased exploration of petroleum reservoirs leading to a surge in oil spills arising from activities like extraction, processing, transportation and storage of petroleum and petroleum products in the oil industry (Olguín et al., 2007). Levy et al. (2010) and Kostka et al. (2011) had reported that hydrocarbon contamination has immensely affected natural resources thus, exerting negative impacts on the natural environment and economic growth.

Environmental pollution caused by petroleum spills goes beyond what can be sensually perceived as there are dire effects that threaten biodiversity, ecosystem and environmental balance owing to leaching, extension and bioaccumulation of contaminants from soil with possible effects on living organisms (Ortínez et al., 2003). Exposure to petroleum can lead to noticeable alteration in physical and chemical features of the soil, limit microbial growth and retard plant development (Vázquez-Luna, 2012).

Certain biological and environmental parameters determine the success of bioremediation strategies aimed at restoring these hydrocarbon polluted environments to their natural state prior to contamination. Sathishkumar et al. (2008) listed some of these parameters to include nutrients, temperature, pH and microorganisms present while Joo et al. (2008) mentioned bioaccessibility/bioavailability of the contaminant, chain length and class of the polluting hydrocarbon. It is easier to put these parameters in check to ensure an effective bioremediation process than to combat the deleterious effect of hydrocarbons and degradation intermediates that arise during or after the process.

Several authors have reported the use of bioremediation as an effective method in eliminating different organic pollutants from soil, thereby reducing their toxicity (Vidali, 2001). Unfortunately, decrease in the degree of petroleum contamination does not always translate to decrease in soil toxicity. Soil toxicity could be worsened by the emergence of intermediary metabolites, partial degradation and persistence of heavy metals (Phillips et al., 2000). Hence, there are some concerns that the products of biodegradation may be more persistent or toxic than the parent compound which may result in poor crop yield when such bioremediated sites are used for plant cultivation. It has been established that contaminants can cause several alterations in plant growth and development (Khan et al., 2008) albeit, the effect metabolic intermediates and residual hydrocarbons from bioremediation have on plant is still being investigated. Moreover, some of these intermediate metabolites, residual petroleum hydrocarbons and heavy metals are carcinogenic and may exacerbate incidences of cancer in humans if they are bioaccumulated in crops and eventually consumed (Jarup, 2003; Khan et al., 2008; Abbas et al., 2011).

Since decrease in total petroleum hydrocarbons, only, cannot provide an overview of the complex process of bioremediation, there is need to investigate the presence of metabolic intermediates arising from the degradation of petroleum hydrocarbons. Chemical analyses in terms of total petroleum hydrocarbon content and polycyclic aromatic hydrocarbon content of soil give information (e.g. bioavailability of contaminant) to help predict the success of bioremediation process however, generation of intermediary metabolites which persists after

the bioremediation process may present even a bigger toxicity problem. Therefore, an understanding of the array of residual contaminants and metabolic intermediates left behind in soil after a bioremediation intervention is important to determine the recovery extent of contaminated soil and the total wellbeing status of the ecosystem. Thus, after a certified bioremediation process, evaluating the presence of these compounds (metabolic intermediates and residual hydrocarbons) and their effect irrespective of their minute concentrations in soil is vital. The combination of data from remediation potential and chemical analysis is required to correctly evaluate the ecological risk present in bioremediated soils.

The use of conventional chemical analysis gives no information about these intermediates as it only gives information about the concentration of residual contaminants. Hence, in this study three (3) petroleum contaminated soil samples that had been certified bioremediated by the relevant regulatory agencies were subjected to gas chromatography-mass spectrometry analysis to determine the array of inherent metabolic intermediates in the samples. Data from this investigation revealed the chemical load of these remediated soil samples.

Materials and Methods

Collection of Soil Samples

Soil samples were collected from bioremediated petroleum hydrocarbon contaminated sites in Ogoniland, Rivers State, Nigeria in October, 2018 for this study. The sampling location is presented in Fig. 1. The bioremediated sites were selected based on their ages (6 months, 12 months, and 18 months after intervention) following remediation certification. Another soil sample was collected from an unpolluted area with undisturbed soil which served as the control. The bioremediated and uncontaminated (control) soil samples obtained were sandy loam in texture. Soil type was young sedimentary soil (histosols) derived from recent alluviation (Onyeike et al., 2002). Surface soil (0–30 cm depth) was taken from each selected bioremediated site and control site using a Dutch soil auger. Forty (40) soil samples were collected at all sampling sites to make four composite samples. Composite sampling was carried out at each of the sites to have a good representation of each sampling site. A fixed grid reference was drawn up for each bioremediated and control site visited and the sampling design involved the utilization of random numbers. At individual sites, the sample size (number of soil samples collected) for each composite sample was ten. Rocks and other particles in the soil samples were removed before mixing to make the composite samples. The composited samples were stored in clean, sterile polythene bags and thereafter, sent to the laboratory for physicochemical analyses in an ice box maintained at a temperature of about 4°C.

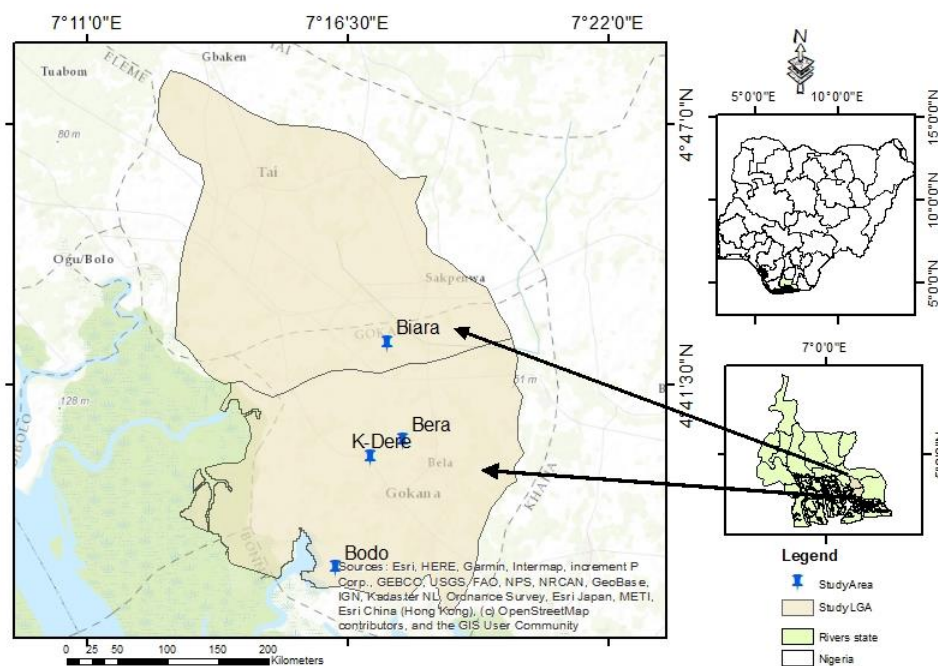


Fig. 1. Map of locations in Ogoniland sampled in this study

Physicochemical Analyses of Soil Sample

Soil pH was determined using a pH meter (Mettler Delta) while the electrometric method was used to determine the electrical conductivity of the soil samples. ASTM D2579 method and ASTM 7503 method were employed to determine the total organic matter and Cation Exchange Capacity respectively. Particle Size Distribution was determined using the ASTM 6913 method while nitrogen content of samples was determined colorimetrically by UV 1800PC spectrophotometer in accordance with EPA 352.1 and APHA 4500-NO₃⁻ B. Phosphate was also determined colorimetrically by UV 1800PC spectrophotometer in accordance with APHA 4500-P-D and Stewart (1989). Total petroleum hydrocarbon (TPH) concentration in the samples were determined with Varian CP 3800 gas chromatography (GC) in accordance with ASTM D5765, EPA 1625 and USEPA 8270B. Polycyclic aromatic hydrocarbon (PAH) content and metabolic intermediates in soil samples were identified using Agilent 6890 GC-MS in accordance with ASTM D7363. For the heavy metals, methods employed were ASTM D8064 (nickel and copper); ASTM D3559 (lead) and ASTM D3557 (chromium) using a flame atomic absorption spectrophotometer.

Data obtained were subjected to statistical analysis using the one-factor Analysis of Variance (ANOVA) to determine if there are significant differences between data obtained from different sites.

Results and Discussion

The physicochemical characteristics of three bioremediated petroleum contaminated soils and an uncontaminated pristine soil obtained from Ogoniland, Rivers State are as presented in Table 1. The three soil samples (6m-AB, 12m-AB and 18m-AB) collected from a crude oil spill site had been certified bioremediated 6 months, 12 months and 18 months prior to sampling respectively by regulatory agencies after an intervention by reclamation outfits. The texture of the bioremediated petroleum contaminated soils and control soil are as presented in Table 1. In all four soils, generally, the sand content was twice higher than the

silt content with clay content being the least. The particle size distribution analysis shows that all soil samples are sandy-loam soil as the proportion of sand ranged from 68.00 – 65.60%; silt between 22.60 – 19.70 %, whereas the clay content in the four soil samples ranged from 14.50 – 10.70 %. The particle size distribution of the four soil samples were similar in terms of their content of sand, silt and clay since they were obtained from the same locality in Ogoniland. Soil texture influences the physical parameters of the soil and plays a very important role in microbial and plant species establishment and development (Chau et al., 2011; Daryanto et al., 2016). The higher percentage of sand and silt in the soil samples suggests adequate porosity and aeration which ensures deleterious contaminants are eliminated through biodegradation and vertical migration (Haghollahi et al., 2016). Colak (2012) had reported low adsorption soil capacity due to low proportion of clay as well as low organic carbon content.

The concentration of nitrogen in soil samples ranged from 73.49 – 35.34 mg/kg with 18m-AB sample having the highest concentration of nitrogen while 12m-AB sample had the least concentration. Inundation of adjoining farmlands during flood events may be responsible for the elevated nitrogen levels in 18m-AB soil sample via horizontal transfer. Sustained use of NPK fertilizer for crop production in farms allows for transfer of these elements to adjoining lands during rainfall events being a consequence of the site's topography. Phosphorus levels in the four soil samples were statistically different ($p=0.05$) and ranged from 0.218 to 0.571 mg/kg. Pristine soil (control) sample had the highest concentration (0.571 mg/kg) of phosphorus while sample 18m-AB had the lowest concentration of phosphorus (0.218 mg/kg). The concentrations of extractable macronutrients, phosphorus, in the bioremediated soil were significantly lower than in uncontaminated soil (Table 1). These relatively lower concentrations of phosphorus could be attributed to its uptake by resident microflora in soil during biodegradation of residual hydrocarbons. Nitrogen and phosphorus are key elements needed for synthesis of proteins, enzymes and nucleic acid during growth of microbes on hydrocarbons. They also influence nutrient-induced community dynamics of native microorganisms and their metabolic interplay (Roy et al., 2018). Oil spill events exert a pressure on the C:N and C:P ratios in soil due to an excessive input of carbon compared to the available micronutrients which facilitates the assimilation of nitrogen and phosphorus by microbes (Xia et al., 2006; Sutton et al., 2013). These two elements are required for eventual utilization of the hydrocarbons as carbon sources and for energy generation.

The pH of 12m-AB and 18m-AB bioremediated soil samples were 6.34 and 6.50 respectively and were slightly lower than pH of uncontaminated pristine soil (7.48) and 6m-AB bioremediated soil (7.40). Bioconversion of residual hydrocarbons to organic acids even after validation of bioremediated sites may have led to the slight acidity of the bioremediated soil samples. Moreover, the TPH and heavy metal contents of crude oil could lead to impairment of gaseous exchange and retention of soil carbon dioxide (Ujowundu et al., 2011). These conditions might have resulted in decreased porosity and conductivity and increased acidity of the bioremediated soils in this study. Soil buffering activities during the bioremediation protocol may be responsible for the neutral pH (7.40) of 6m-AB soil sample. Soil pH has a great influence on microbial activity and ultimately bioremediation success or rate as most microorganisms can thrive only within a certain pH range. For instance, neutral

pH of 7 might be optimal for the degradation of chemicals by microbes however, pH range in the order of 6–8 may also be acceptable for effective microbial attack. The pH of soil samples used in this study fell within this range. Rousk et al. (2010) had observed high microbial activity in neutral soils and lower microbial activity in acidic soils whereas, Itah and Essien (2001) had reported bacteria that thrive in alkaline or acidic soil condition. In a study carried out by Mukut and Arundhuti (2012), soil samples whose pH was adjusted to 4.5 and 7.5 had significant biodegradation of petroleum hydrocarbons unlike soil samples whose pH was adjusted to 3.5. Depending on other soil features, a change in pH of a soil contaminated with petroleum may cause contaminants to precipitate and become highly mobile or make contaminants to adsorb to the soil and inhibit degradation (Ajoku and Oduola, 2013). Previous reports have shown that pristine tropical garden soil generally has a pH of about 7.15 (Choppala et al., 2018). A study by Verstrate et al. (1975) emphasized optimal activity for microbial degradation at a pH of 7.4 and considerable inhibition at pH 4.5 and 8.5. Nevertheless, the pH of the three bioremediated soil samples in this study were within the range of 6 and 8 which suggests that bacterial degradation activities will be sustained provided favorable conditions exist in soil. Favorable soil pH is important in ensuring sustained microbial metabolism in soil in order to facilitate the extinction of the residual hydrocarbons in the soil (Atlas and Bartha, 1992). Moreover, nutrient availability in soil or water may be influenced by pH.

The electrical conductivity of the bioremediated soil samples was considerably lower when compared to the uncontaminated soil sample. Pristine soil had the highest electrical conductivity value of 8.00 $\mu\text{S}/\text{cm}$ while 6m-AB and 12m-AB soil had the least value of 2.00 $\mu\text{S}/\text{cm}$. Likewise, the concentrations of sodium, calcium and magnesium were lower than was obtained for the uncontaminated soil sample thus, suggesting that petroleum contamination and eventual biological treatment of the soil altered the soil's physicochemical characteristics. The cation exchange capacity (CEC) comprises of four (4) compounds which are potassium, sodium, calcium, and magnesium. For sodium, pristine soil had the highest value (0.4613 mg/kg) while 18m-AB had the lowest value (0.3056 mg/kg); for calcium, the highest value of 2.864 mg/kg was obtained from pristine soil sample while the least value of 0.041 mg/kg was obtained from 12m-AB sample; for magnesium, pristine soil had the highest value of 0.3831 mg/kg whereas the least value (0.1438 mg/kg) was obtained from 12m-AB. Potassium was not detected in uncontaminated and bioremediated soil samples. The reduction in the concentrations of sodium, calcium and magnesium which are essential nutrients and suitable terminal electron acceptors may have affected the indigenous microbial growth and metabolism (Ujowundu *et al.*, 2011). The lower conductivity values of 2.0 to 4.0 $\mu\text{S}/\text{CM}$ in bioremediated soils when compared to 8.0 $\mu\text{S}/\text{CM}$ in the uncontaminated soil may be attributed to the reduction in the nutrient content of the bioremediated soils. There is a positive correlation between available nutrient and electrical conductivity. The range of values for total organic matter (TOM) was 0.095 – 1.232 % with 6m-AB soil having the least value; whereas pristine soil and 12m-AB had the highest value of 1.232 %. There were no significant differences ($p=0.05$) between the total organic matter (TOM) content of the uncontaminated soil and the bioremediated soil samples though, the TOM in uncontaminated soil was slightly higher than was obtained in bioremediated soil samples. The annihilation of plant species soon after the oil spill that occurred in bioremediated sites and the enhanced

microbial activities as a result of the bioremediation protocol may have led to the drop in TOM content of these soil samples.

Table 1. *Physicochemical Characteristics of Soils obtained from Ogoniland, Rivers State.*

Parameters	Sample Identity			
	Control	6m-AB	12m-AB	18m-AB
pH	7.48	7.40	6.34	6.50
Electrical Conductivity, EC ($\mu\text{S}/\text{CM}$)	8.00	2.00	2.00	4.00
Total Organic Matter, TOM (%)	1.232	1.095	1.232	0.958
Cation Exchange Capacity, CEC				
	Potassium, K (mg/kg)	<0.001	<0.001	<0.001
	Sodium, Na (mg/kg)	0.4613	0.3468	0.3646
	Calcium, Ca (mg/kg)	2.864	0.102	0.041
	Magnesium, Mg (mg/kg)	0.3831	0.1663	0.1438
Particle Size	Sand	65.60	68.4	65.80
Distribution, PSD (%)	Silt	22.60	20.60	19.70
	Clay	11.80	11.00	14.50
Nitrogen (mg/kg)		38.007	46.940	35.340
Phosphorus (mg/kg)		0.571	0.480	0.283
Total Petroleum Hydrocarbon, TPH (mg/kg)	BDL	161.25	51.72	91.50
Polyaromatic Hydrocarbon, PAH (mg/kg)	BDL	BDL	BDL	BDL

The TPH contents in bioremediated petroleum contaminated soil samples encountered were 161.25 mg/Kg, 51.72 mg/Kg and 91.50 mg/Kg for 6m-AB, 12m-AB and 18m-AB respectively. These values exceed the EGASPIN recommended TPH target value of 50 mg/kg however, they are below the intervention level of 5,000 mg/kg. The uncontaminated pristine soil sample had no trace of residual TPH. The higher-than-target value residual TPH content obtained for these bioremediated soils suggests that the reclamation process fell short of achieving the set objectives of regulatory agencies. The relatively higher TPH concentration obtained in 6m-AB could be attributed to its age status (6 months after intervention) when compared to the samples obtained from other sites that had fallowed for 12 months and 18 months after intervention. During site fallowing, degradation of residual petroleum hydrocarbons is sustained by surviving microorganisms as long as conditions remain favorable for their growth despite site demobilization. This may account for lower residual TPH values obtained for 12m-AB and 18m-AB. TPH degradation may happen naturally by native microorganisms with degradation rate of 77% after 30 months of contamination (Rhykerd et al., 1999). Biodegradation of target compounds by indigenous microbial communities is frequently considered to be the primary mechanism for attenuation of contaminants (Declercq et al., 2012). Stimulated or not, indigenous microorganisms capable of petroleum hydrocarbon biodegradation could have a crucial impact on remediation, especially if site was exposed prior to contamination (Bento et al., 2005; Sabaté

et al., 2004). However, the composition of the hydrocarbons and the prevailing environmental conditions affect the composition and competence of the inherent microbial population (Bento et al., 2005). Hence, concentrations of the TPH obtained in sites studied despite being certified reclaimed can render conditions in soil unsatisfactory for the growth of plants and microorganisms.

Even more worrisome is the load of intermediate metabolites arising from the degradation of TPH by microbes. Screening of the soil samples using gas chromatography-mass spectrometer revealed a number of metabolic intermediates in bioremediated soil samples when compared to the uncontaminated pristine soil (control). The array of metabolites identified is as presented in Table 2. Some of these metabolites are known carcinogens and are deleterious to plant growth. Their presence in the bioremediated soil is indicative of the unhealthy status of the soils in terms of agricultural productivity. One of the main aims of polluted site reclamation especially in Nigeria is the resumption of farming activities and animal husbandry on such sites (UNEP, 2011; Umukoro, 2012) since most locals in affected areas depend on agriculture for survival. Hence, the presence of these metabolites in the reclaimed petroleum contaminated sites may hinder plant growth and agricultural productivity.

Most of the metabolites detected in bioremediated soil samples are efflorescent chemicals with the capacity to pose a threat to human health, aquatic and terrestrial ecosystems and wild life diversity (Eggen et al., 2010). Many of these organic compounds-halogenated aliphatic and aromatic compounds, nitrogen containing compounds, and phthalate esters, are known carcinogens and mutagens (Alimba et al., 2016). They have been prioritized on the list of hazardous substances and are deleterious to cells even at minute concentrations (Fay and Mumtaz, 1996; ATSDR, 1997). These metabolites have also been implicated in the causation of cytotoxicity and DNA damage in the model cells. For instance, dibutylphthalate and diisobutylphthalate (phthalate esters) detected in soil samples in this study had induced DNA single-strand breaks in nasal mucosa and pharyngeal epithelia cells in previous reports (Kleinsasser et al., 2000). Likewise, DNA double-strand breaks were induced by Bisphenol A in mutant chicken DT40 cell line deficient in DNA repair pathways (Lee et al., 2013). Other metabolites like trifluoromethyltrimethylsilane is known to cause skin and eye irritation, respiratory irritation, and central nervous system depression in humans when exposed to this chemical (Federal Register, 2012). Moreover, some of these metabolites present in the bioremediated soil samples are stable lipophilic compounds and hence may possess bioaccumulation potentials in plants which will result in their biomagnification through food webs via accumulation in fat-rich tissues of higher trophic animals including humans. Consumption of such food materials may result in cancers and other ailments (Jarup, 2003; Khan et al., 2008; Abbas et al., 2011). A previous report had shown that organic compounds in bioremediated soils were readily accumulated in cultivated edible vegetables (Shagal et al., 2012), and also led to contamination of underground and surface potable water supply around the locality of the oil spill sites (Melnik et al., 2014; Sanchez-Chardi et al., 2007; Someya et al., 2010). This suggests that bioremediated soils, water sources around contaminated sites and edible crops cultivated on such soil may be possible human exposure routes to these chemical mixtures. It has been shown in previous reports that people working in and living around landfill facilities harbored higher concentrations of toxic metals and

organic pollutants in their blood and breast milk than control population (Devanathan et al., 2012; Malarvannan et al., 2009). More so, some of these compounds detected in bioremediated soil samples may be endocrine disrupting chemicals capable of impairing reproduction and developmental processes leading to increase carcinogenesis (Eggen et al., 2010; Vilavert et al., 2012). Variations in the concentrations of the detected organic compounds in the various soil samples indicate that the constituents of the soil may depend on the type of oil spilled, the age and the metabolic activities inherent in the contaminated soil (Eggen et al., 2010; Vilavert et al., 2012) and these vary from one contaminated site to another.

Table 2. Array of Metabolites Identified in Various Soil Samples Used in this Study

Control	6m-AB	12m-AB	18m-AB
1,1'-Biphenyl, 2,4-dichloro-2',5'-dimethyl-	1-Heptyn-4-ol	1,3-Dioxolane, 2-(phenylmethyl)-	1-Ethenyl-3-(1-hexenyl)-4-trimethylsilylcyclopentane
1H-Pyrazole-3-carboxylic acid, 1-[(3-chlorophenyl)methyl]-, methyl ester	1-Hexen-4-ol, 1-chloro-3,5-dimethyl-	1,3-Dioxolane, 2-(1-phenylethyl)-	1-Hexen-4-ol, 1-chloro-3,5-dimethyl-
1-Naphthalenecarboxylic acid, 8-bromo-	1,3-Bis-t-butylperoxy-phthalan	1,3-Dioxolane, 2-(3-bromo-5,5,5-trichloro-2,2-dimethylpentyl)-	1,3-Dioxolane, 2-(3-bromo-5,5,5-trichloro-2,2-dimethylpentyl)-
1-(2-Methoxyethoxy)-2-methyl-2-propanol, methyl ether	1,3-Dioxolane, 2-(3-bromo-5,5,5-trichloro-2,2-dimethylpentyl)-	[2,6'-Bi-2H-1-benzopyran]-4(3H)-one, 3',4'-dihydro-3,5,7-trihydroxy-5'-methoxy-2',2'-dimethyl-, (2S-trans)-	2-Butanol, 3-methyl-
1,3-Bis-t-butylperoxy-phthalan	2-Butanone, 3-methoxy-3-methyl-	2-Butanol, 3-methyl-	2-Ethoxy-3-chlorobutane
1,3-Dioxolane, 2-(1-phenylethyl)-	2-Ethoxy-3-chlorobutane	2-Butanone, 3-methoxy-3-methyl-	2-Ethyl-3-ketovaleate, 2TMS derivative
1,3-Dioxolane, 2-(2-propenyl)-	2-Mercaptoethanol, TMS derivative	2-Ethoxy-3-chlorobutane	2-Vinylethyl acetate
1,3-Oxathiolane-4-carboxylic acid, 2-imino-5-phenyl-, ethyl ester	2-Vinylethyl acetate	2-Phenylisopropanol, TMS derivative	3,5-Dimethyl-5-hexen-3-ol
2-Propanamine, N-methyl-	2,2-Dimethyl-propyl 2,2-dimethyl-propanesulfinyl sulfone	2-Propanamine, N-methyl-	5-Methyl-4'-hydroxy-2-benzylidene-coumaran-3-one
2-Vinylethyl acetate	2,3-Dihydro-2-methyl-4-(4-methylphenyl)-1H-1,5-benzodiazepine	3-Hexene, 1-(1-ethoxyethoxy)-, (Z)-	9,9-Dichloro-9-silafluorene

Table 2. Array of Metabolites Identified in Various Soil Samples Used in this Study (Continued)

Control	6m-AB	12m-AB	18m-AB
2,3-Dichlorothiophene-5-sulfonyl chloride	2-[4-Chloro-trans-styryl]-4-chloropyrimidine	3-Pentanol, 3-methyl-	Benzenemethanol, _-[(methylamino)methyl]-
3-(1,2-Dibromoethyl)-1,1,2,2-tetrafluorocyclobutane	2,6-Dodecadienoic acid, 10-(bromoacetoxy)-11-methoxy-3,7,11-trimethyl-, methyl ester	3,4-Dimethyl-5-hexen-3-ol	Butane, 1-chloro-4-(1-ethoxyethoxy)-
3,3-Dichloropropyne	3-Buten-2-ol	3,6-Bis(trimethylsilyl)-1,4-cyclohexadiene	Methylarsine dibromide
3-Bromo-2-quinolinecarboxamide	3-Pentanol, 3-methyl-	4-Pyridinamine, 3,5-dibromo-	Methyl p-coumarate, TMS derivative
3-Methoxy-3-methylbutanol	3,4-Dimethyl-5-hexen-3-ol	5-(2-Methoxypropan-2-yl)-2-methyl-2-vinyltetrahydrofuran	Silane, (2-ethyl-4-methylene-1-cyclopenten-1-yl)trimethyl-
3-Pentanol, 3-methyl-	3,6-Bis(trimethylsilyl)-1,4-cyclohexadiene	5-Methyl-4'-hydroxy-2-benzylidene-coumaran-3-one	Silane, 9-anthracenyltrimethyl-
5-Methyl-4'-hydroxy-2-benzylidene-coumaran-3-one	4-Methoxy-4-methyl-2-pentanol	6,11-Dihydro-8-methoxy-1-benzopyrano[4,3-b]indole	Silane, trimethyl(1-phenylethyl)-
Benzyl alcohol, _-(1-(dimethylamino) ethyl)-	4-Pyridinamine, 3,5-dibromo-	9,9-Dichloro-9-silafluorene	Trifluoromethyltrimethyl silane
Methanol, chloro-, acetate	5-Methyl-4'-hydroxy-2-benzylidene-coumaran-3-one	Benzyl alcohol, _-(1-(dimethylamino)ethyl)-	
Methylarsine dibromide	5-Hexen-3-ol, 3-methyl-	Butane, 1-chloro-4-(1-ethoxyethoxy)-	
Methyl p-coumarate, TMS derivative	6,11-Dihydro-8-methoxy-1-benzopyrano[4,3-b]indole	Butanoic acid, 2-hydroxy-2-methyl-, methyl ester	
Propanoic acid, 3-chloro-	Bromo-dragonFLY	Methanol, chloro-, acetate	
Propane, 1,1-dimethoxy-	Butane, 1-chloro-4-(1-ethoxyethoxy)-	Methyl p-coumarate, TMS derivative	

Table 2. *Array of Metabolites Identified in Various Soil Samples Used in this Study (Continued)*

Control	6m-AB	12m-AB	18m-AB
Propane, 2-methoxy-2-methyl-	Butane, 2-methoxy-2,3,3-trimethyl-	Pyrimidine, 5-bromo-2,4-bis(methylthio)-	
Pyrimidine, 5-bromo-2,4-bis(methylthio)-	Methyl 10-(chloroacetoxy)-11-methoxy-3,7,11-trimethyl-2,6-dodecadienoate	Silane, (2-ethyl-3,3-dimethyl-4-methylene-1-cyclopenten-1-yl)trimethyl-	
Silane, 9-anthracenyltrimethyl-	Methyl p-coumarate, TMS derivative	Silane, 9-anthracenyltrimethyl-	
Silane, trimethyl(1-phenylethyl)-	Propanoic acid, 3-chloro-	Silane, tetramethyl-	
Trimethyl(3,3-difluoro-2-propenyl)silane	Propane, 2-methoxy-2-methyl-	Silane, trimethyl(1-phenylethyl)-	
Trifluoromethyltrimethylsilane	Pyrimidine, 2-(3,5-dimethylpyrazol-1-yl)-5-phenyl-	Spiro[(5-bromoacenaphthen-1-one)-2,2'-(5',5'-dimethyl-1',3'-dioxane)]	
	RS-2,3-hexanediol	(SR)- or (RS)-4-methyl-2,3-pentanediol	
	Spiro[(5-bromoacenaphthen-1-one)-2,2'-(5',5'-dimethyl-1',3'-dioxane)]	Trifluoromethyltrimethylsilane	
	Trimethyl(3,3-difluoro-2-propenyl)silane	Trimethyl(3,3-difluoro-2-propenyl) silane	

Some of these contaminants usually bind to the soil particles and are slowly released into the environment (Schuhmacher et al., 1998; Lah et al., 2008). Heavy metals (nickel, cadmium, lead, and copper) were below detectable limits in bioremediated petroleum contaminated soil samples as well as in the control soil sample. This was unexpected since heavy metals cannot be degraded and some of them have been associated with petroleum and usually found at crude oil spill sites. Nonetheless, their non-detection in the reclaimed spill sites may be attributed to vertical and horizontal migration from top soil due to precipitation and flood events. The heavy metal content of the reclaimed soil samples was within the EGASPIN prescribed limits as shown in Table 3.

Table 3. Heavy metal concentrations in bioremediated soil samples obtained from Ogoniland

Heavy Metals	Sample Identity					
	Target Limit	Intervention Limit	Control	6m-AB	12m-AB	18m-AB
Nickel, Ni (mg/kg)	35	210	0.067	<0.001	<0.001	0.054
Copper, Cu (mg/kg)	36	190	0.035	0.016	<0.001	0.005
Lead, Pb (mg/kg)	85	530	0.04	0.11	0.07	0.05
Cadmium, Cd (mg/kg)	0.80	12	<0.001	<0.001	<0.001	<0.001

Conclusion

The TPH content of the bioremediated petroleum contaminated soil samples varied widely with that of pristine soil as TPH content was below detectable limits in the uncontaminated pristine soil whereas, in the bioremediated soils, TPH content was above the target value recommended by EGASPIN. However, PAH and heavy metals were below detectable limits in both uncontaminated and bioremediated soils. A wide array of metabolites was identified in bioremediated soils when compared to the uncontaminated pristine soil. Some of the identified metabolites and residual contaminants are known carcinogens and eco-toxicants and maybe deleterious to plant growth thus, suggesting the unhealthy status of the bioremediated soils for agricultural productivity. There is need to encourage further natural attenuation regime in bioremediated sites in order to ensure the obliteration of the residual contaminants and metabolic intermediates in soil before the return to agricultural activities on such sites.

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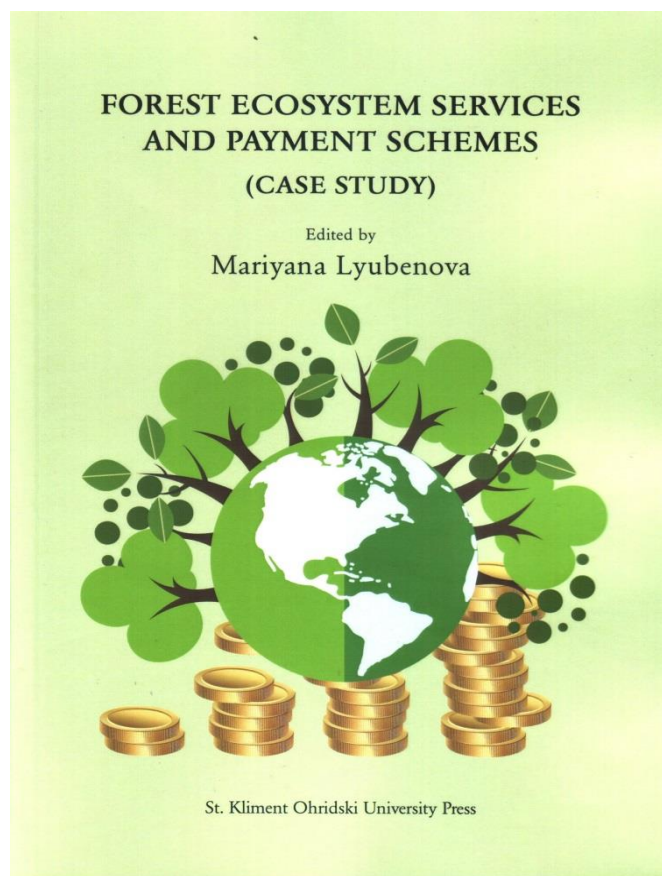
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